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The effect of ink/fountain solution emulsion of paper permanence

Thomas H. Spotts

THE EFFECT OF INK/FOUNTAIN SOLUTION EMULSION ON PAPER PERMANENCE

by

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requirements for the degree of Master of Science in the
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ABSTRACT

The permanence of printed documents and books appears to be primarily dependent on paper stability. Other researchers implicate pH as a major factor in the deterioration rate of paper and acidity as major the cause of this deterioration. During the lithographic printing process, ink is in direct contact with fountain solution, which can be acidic or alkaline. Fountain solution is a mixture of water and chemicals used to keep the non-image areas of a lithographic plate moist. On press the intimate contact of ink with fountain solution creates a fountain solution-in-ink emulsion. The emulsion used here is a stable suspension of fountain solution droplets within the ink. The objective of this study was to determine if ink/fountain solution emulsion, which is printed on paper during lithographic printing, affects the rate of deterioration of paper.

The stability of four commonly available papers was observed. These paper types were groundwood, publication grade, coated book, and uncoated book. Samples of the four paper groups were printed with four different ink formulations. The ink formulations were ink, ink and distilled water, ink and acidic fountain solution, and ink and alkaline fountain solution. Samples of the unprinted and printed paper were subjected to an accelerated - aging process by heating the samples for 72 hours at $100^{\circ}C$. The properties of unaged and aged papers were evaluated by pH determination, folding endurance, and tearing resistance. On the basis of statistical analysis of the data, inferences were made about the effect of

the ink formulations on the paper properties.

This experiment indicates that ink/fountain solution emulsion did affect the paper pH, but this effect is due to the ink with little change in pH due to the addition of acidic or alkaline fountain solution to the ink. The results of folding endurance and tearing resistance tests after accelerated aging established no clear pattern of variance that would indicate the differences observed in these properties were due to the pH change associated with the ink/fountain solution emulsions. Several unexpected occurrences were exhibited by this experiment. These include: groundwood was the paper least affected by the aging process; the pH of coated paper increased with the application of ink/fountain solution emulsion; a decrease in tearing resistance was associated with alkaline fountain solution.

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with a major in Printing Technology has been approved
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CHAPTER I. INTRODUCTION

Some printed paper products are discarded or destroyed immediately after serving their intended purpose, while others are expected to retain usable qualities over an extended period of time. In the first case, the usable life of the paper need not be long and paper deterioration is not a major concern. Books, documents, and records are in the second category, requiring a paper that has a certain degree of permanence, so paper deterioration is of major concern. Often when discussing paper products of this category, the terms permanence and durability are used synonymously. Both permanence and durability are necessary for books, records, and documents, but they mean different things. Suitable definitions of permanence and durability for this study are given by W. H. Bureau in Graphics Arts Monthly, April 1971:

> Permanence refers to the extent to which a paper will retain its original properties upon storage. The extent to which a paper is permanent is generally measured by ... the loss in the brightness or whiteness after aging .. and the percentage of its original strength after normal or accelerated aging as indicated by fold and tear tests. Durability refers to the extent to which a paper will resist deterioration when subjected to use or handling.

Paper permanence involves many factors. Not only is it affected by the pulping and paper making process, and impurities in the sheet, but by storage conditions such as temperature, relative humidity, light, and atmospheric pollutants. In order to predict paper permanence, the manufacturing history of the paper and its intended use or storage conditions must be known. It is not possible to consider all factors, therefore, laboratory investigations of paper permanence study a variable and its effect on paper deterioration or degradation in a controlled, accelerated-aging atmosphere. By evaluating different properties after accelerated aging, an order or arrangement of relative permanencies might be evident and inferences can be drawn on how the paper's properties might be affected under certain storage conditions over time.

As a number of studies in the past have determined acidity to be a cause of paper deterioration (Notes 1, 2, 3, 4), the pH test is often recommended as the best single indication of paper permanence.[5] The loss of paper permanence corresponds with a decrease in the paper pH. Therefore, specifications for an "archival" quality paper (permanent/durable paper) include a minimum pH value for the paper (usually about 7.5).

In the lithographic printing process, which is one of the major printing methods used today, the differentiation between image and non-image (printed and non-printed) areas is made chemically. The lithographic plate is planographic, that is, there is no significant physical difference between the height of the image and non-image area, and chemical changes on the plate surface make the image area ink-receptive and the non-image area water-receptive. The dampening or fountain solution used to keep the non-image area moist, so as not to accept ink can be acidic. Since lithographic ink works in the presence of a dampening solution during a press run, it must be able to "pick up" or emulsify up to 35% of its weight in fountain solution without impairing working properties or ability to print cleanly.[6] As stated in the study by Aage Surland;

> ...lithography depends on the ink's ability to emulsify the dampening solution which, during the process, is inavoidably applied to the surface. The medium which is printed on the substrate is not the ink as was applied to the press, but an emulsion of aqueous dampening solution in the continuous hydrophobic phase.[7]

Statement of Problem:

Books, documents, and records require paper that is permanent and durable. Although care is taken to choose a paper suitable for the purpose, little consideration is given to how the printing process affects the properties of the paper.

Paper deterioration is a major factor in books and document permanence and can be accelerated by the presence of acidity in the paper. The acidity present in the paper might be changed by an external source, ink/fountain solution emulsion applied to it during the lithographic printing process. The relation of ink/fountain solution emulsion to paper permanence should be established.

The purpose of this investigation is to study the effect of ink/fountain solution emulsion on paper permanency.

FOOTNOTES FOR CHAPTER I

1. R. S. Smith, "Paper Impermanence as a Consequence of pH and Storage Conditions", _Library Quarterly_ 39 (April, 1969): 157.

2. Gosta Hall, "Permanence of Paper", _Paper Trade Journal_ 82 (April 8, 1926): 52-8.

3. R. H. Rasch, M. B. Shaw and G. W. Bicking, "Highly Purified Wood Fibers as Paper-Making Material", _Bureau of Standards Journal of Research_ 7 (August 25, 1931): 765-82.

4. William K. Wilson, Jack L. Harvey, John Mandel and Thelma Worksma, "Accelerated Aging of Record Papers Compared with Normal Aging", _TAPPI_, 38 (September, 1955): 543-48.

5. David D. Roberson, "The Evaluation of Paper Permanence and Durability", _TAPPI_, 59 (December, 1976): 68.

6. Robert F. Reed, _What The Lithographer Should Know About Ink_, (Pittsburg: Graphic Arts Technical Foundation, 1960): p. 12.

7. Aage Surland, "A Laboratory Test Method For Prediction of Lithographic Ink Performance", _TAGA Proceedings_, 1980, p. 226.

CHAPTER II. BACKGROUND AND LITERATURE

For the purpose of this thesis, paper deterioration is defined as a gradual worsening of the quality of paper. The many causes of paper deterioration can be placed in the categories of physical causes, chemical causes, and biological factors. Physical causes involve the careless mechanical handling of the paper, such as the tearing or ripping of a paper in a book. Chemical causes include acidity that degrades (reduces in quality or deteriorates) the paper and photochemical attack, including oxidation of cellulose (the sustance that constitutes the fibers that make up the raw material for paper) which can cause the discoloration of paper. Biological factors include mold growth, fungus, insect attack, and rodent attack.

Paper deterioration during aging is the result of a combination of factors. For example, a high quality sheet of paper containing long fiber raw material and having a neutral or slightly alkaline pH, can deteriorate rapidly if stored in an environment where the temperature and humidity cycle from high to low throughout the year and where atmospheric pollutants are present. Likewise, a low quality sheet of paper containing groundwood and having an acidic pH, may last longer if stored in an environment where temperature and humidity are controlled and the air is filtered. Because past research has determined acidity to be a significant cause of paper deterioration (see Notes 1, 2, 3, 4, Chapter 1), this thesis focused on acidity and its effect on paper properties after accelerated aging.

The recognition of acidity as a cause of paper deterioration and concern about paper impermanence date back to the early 1800's. Among the causes of paper deterioration proposed at that time by John Murray, a Scottish lecturer and writer, were excessive acidity, overbleaching, and poor-quality raw materials.[2] However, investigations done in the twentieth century definitely link acidity and paper deterioration.

Several studies, conducted during the early 1900's concluded that acidity played a role in paper deterioration. In the five-year span between 1904 and 1909, the U. S. Department of Agriculture made an investigation to determine suitable papers for government purposes. Free acids and soluble salts which may yield acids were cited as causes of embrittlement and weakening of paper.[3] During the early 1920's, the Swedish Government Testing Institute conducted a series of investigations on paper deterioration. Based on the results of tests, it was concluded that increased paper acidity promotes increased decomposition of cellulose.[4] Around the same period of time the U. S. National Bureau of Standards was also investigating paper permanence. Rasch, Shaw, and Bicking, who worked with highly purified wood fibers in 1931, proposed that paper acidity be controlled to produce a stable paper because the excess of alum (from the alum-rosin sizing method) resulted in reduced stability of the paper in the accelerated aging test.[5]

Perhaps the most recognized work done on book and paper permanence is the studies done by the Barrow Research Laboratory of Richmond, Virginia, during the 1950's and 1960's. This laboratory did extensive investigations on books discarded from area libraries and suggested that acid in paper is a major cause of paper deterioration. As a result of these studies, the Barrow Research Laboratory recommended specifications for uncoated permanent and durable papers in which a minimum pH value was emphasized.[6]

Background

In order to better understand paper deterioration, a brief description of terms "acid" and "base" is first necessary. For the purpose of this thesis, acid will be defined as a compound or substance that can release or donate hydrogen ions (H) when dissolved in water or an ionizing solution, and base will be defined as a substance or compound that produces hydroxide ions (OH-) in solutions, or accepts hydrogen ions.

Another term, used in connection with acids and bases, is pH. For instance, when referring to the acidity level of paper, a pH number is often used. The phrase "pH of paper" is a misnomer, as it is actually a measurement of the pH of the water extract of paper, and not of the paper itself. The pH scale was introduced by a Danish chemist named Sorensen and provides a number to describe acidity.[7] Since water solutions of dilute acids and bases are so often used, it is a convenient and simple way to designate the acidity or alkalinity of the solutions.[8] The abbreviation pH, refers to "Potential of Hydrogen", and the scale of numbers expresses the hydrogen ion (H^+) concentration. So pH is actually a measurement of hydrogen ions, not acidity, but it provides a simple way to indicate acidity.

The pH scale indicates the concentration of hydrogen ions (in moles per liter) of an aqueous solution as a power of 10 ($pH = -\log (H^+)$). The scale range is from 1 to 14, 1 being most acidic, 7 being neutral, and 14 being most alkaline or basic.

As stated previously, a pH number in reference to paper is not a measurement of acidity in paper, but rather an indication of the acidity of the water extract of the paper. Acid-catalyzed hydrolysis being a significant cause of paper deterioration, (see pp. 9, 10) pH is often used as an indicator of potential paper permanence. As the pH of the paper decreases, the paper is less permanent in quality.[9]

It has been established that paper of low pH embrittles and changes physical properties during storage or aging.[10] To understand better why acid affects paper during aging and why physical strength decreases, a brief discussion of reactions that occur during the aging of cellulose and paper is provided.

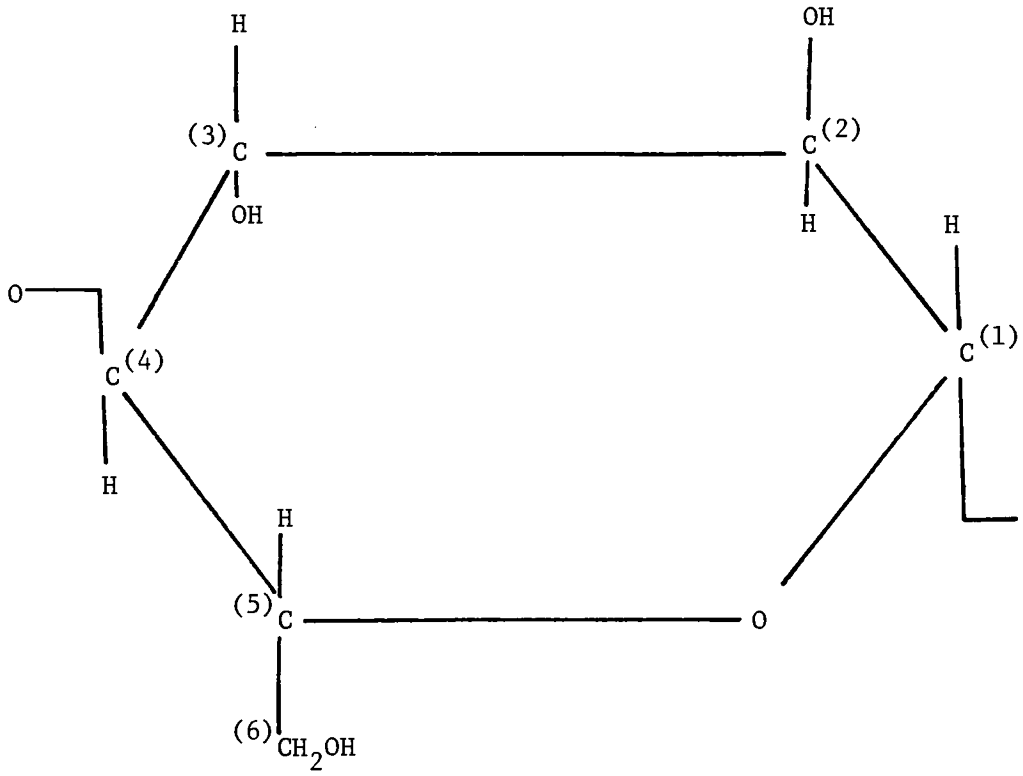
Testing shows that certain chemical and physical reactions occur during the aging of paper. However, such tests indicate only that a change occurs, seldom why this change takes place.[11] According to a report by Wilson and Parks, prepared for the National Bureau of Standards (NBS), among possible reactions during the aging of paper or cellulose are hydrolysis, oxidation, and cross-linking. An analysis of these reactions explain some of the physical and chemical changes observed during the natural or accelerated aging of paper.

Hydrolysis is a reaction in which a chemical bond is broken and water is added, hydrogen ions to one part and hydroxide ions to the other part.[12] The reaction can create an excess of hydrogen or hydroxide ions, depending on the substance. There are acetal linkages present in cellulose that are stable in neutral and alkaline media, but easily hydrolyzed in acid, the rate of hydrolysis increasing with the hydrogen ion activity. During the accelerated or natural aging of paper, acid catalyzed hydrolysis breaks chemical bonds in accessible areas of cellulose, reducing the degree of polymerization (DP) or, put simply, breaking the long chains of cellulose. Tests sensitive to fiber bond or fiber deterioration (due to the decrease in DP), such as fold and tear, would show a decrease. Organic acids could be produced from carbohydrate structures during hydrolysis and thus increase the acidity of the paper during aging.[13]

An oxidation-reduction reaction is a common reaction in which electrons, or control of valence electrons (electrons in the outermost shell of an atom, regarded as being responsible for the chemical reactions of an element), pass from one atom to another.[14] The atom losing the electrons or control of them is said to be oxidized, while the atom gaining is reduced. The previously cited NBS study by Wilson and Parks suggests the possibility of oxidation of carbohydrate structures during the aging of paper. This is based on the generally accepted cellulose structure (See Fig. 1). It involves the oxidation of alcohol groups at different carbon locations of the cellulose structure to aldehyde, carboxyl, or ketone groups. In the case of natural aging of paper, oxygen or ozone would act as the oxidant. The oxidation results in a decrease of DP, partly because of increased sensitivity of the oxidized structure to hydrolysis, and so reduces physical properties.[15]

Cross-linking results when new chemical bonds are formed between

Figure 1. Generally accepted cellulose structure, Wilson, Parks, "An Analysis of the Aging of Paper" Restaurator, 3 (1979), pg. 41.



polymer chains (chains formed by linear polymerization). It occurs in both moist and dry atmospheres, and according to Wilson and Parks, results from conditions that can be described as accelerated aging. Physical properties such as fold, tear, and burst will decrease with the occurance of cross-linking.[16]

Included is a table from the National Bureau of Standards report that shows the effects of reactions on various paper tests (see Table 1).

Knowledge of the chemical reactions involved in the deterioration of paper is not yet complete and, therefore, all factors which determine paper permanence are not clearly defined. However, it is indicated that the degradation of book paper is in a major part due to hydrolysis.[17,18,19,20,21] Hydrolysis shortens the length of the cellulose polymer by randomly breaking the chain which, in turn, causes a decrease in physical properties. The rate of hydrolysis degradation of cellulose in paper is determined by the hydrogen ion concentration.[22] Therefore, the acidity present in the paper resulting from manufacturing or other sources is a major factor in the hydrolysis or rate of hydrolysis of the cellulose. In addition, products resulting from the degradation of cellulose may increase the acidity of the paper and further promote degradation.[23]

Justification

In a study published in a 1972 issue of the Restaurator, Richard D. Smith compared paper from books stored in different locations. Identical copies of books from three different libraries, one in New York City, one

TABLE 1. REACTIONS, OR CHANGES, THAT MIGHT OCCUR DURING AND ACCELERATED AGING OF PAPER, AND THEIR EXPECTED EFFECTS ON VARIOUS TESTS.

	Reaction or Change; P = primary, S = Secondary					
Test	Hydrolysis		Oxidation		Cross-linking	
	P	S	P	S	P	S
Acid, H^+		+	+		na	
Fold	-		-		-	
Tear	-		-		-	

+ indicates an increase

- indicates a decrease

na not applicable

Information from table by Wilson, Parks, "An Analysis of the Aging of Paper", Restaurator, 3 (1979), pg. 47.

in Chicago, and one in Appleton, Wisconsin, were examined. The atmosphere in New York and Chicago is more polluted than Appleton, as shown by the Environmental Protection Agency data presented in the article. It was found that the margins of pages in books stored in New York and Chicago were more acidic than the center of the pages. This is believed to be the result of the polluted atmosphere causing the edges of the paper to become more acidic. However, in books stored in Appleton, pages were found to be more acidic at the center than at the margins. Smith speculated that this resulted from acidic products of ink degradation. Also cited by Smith were the findings of the Barrow Research Laboratory that supported this observation. In examining copies of books discarded by the Richmond, Virginia, area libraries (considered to be in a less or non-polluted atmosphere), the Barrow Laboratory found that in three out of five books the printed leaves were more acidic and attributed this to the ink medium degrading and forming acidic oxidation products. This suggests that the ink medium printed on paper might affect the stability of that paper.

Printing inks based on linseed or similar oils may form acidic products upon degradation. In a study of the effects of dried ink on the drying of overprinted ink, Paul Hartsuch noted that different ink varnishes had the effect of a retardant if dried and aged for a period of time, when another ink is printed over the first.[24] The retarding material in the aged inks was thought to be acidic, produced upon degradation of the inks. Assuming that certain inks produce acid by-products upon aging or degradation, the acids may affect the acidic level of the paper (given, of course, that any effect would be dependent on the amount of ink). If printed by lithography, the ink also picks up some fountain solution which may be acidic, and this may also contribute to the acidity. If the acidic level of the paper were altered, this may or may not have an effect on the deterioration of paper and therefore affect the physical properties and stability during storage or aging.

In a presentation to a 1973 seminar on Conservation of Library and Archival Materials, A. E. Werner made mention of ink as an extrinsic source of acidity to paper. Although he felt it a minor source of acidity when compared with atmospheric pollution, writing and printing inks were discussed. "Printing inks based on linseed oil may produce acidic components."[25] Again, reference to the Barrow Research Laboratory work is made.[26]

It has been recognized that commonly used early writing inks contained acids. As many early records were preserved in manuscript form, the writing ink used might influence the permanence of the record. This was studied by Zimmerman, Weber, and Kimberly in 1935 and it was found that certain writing inks did deteriorate the paper more quickly in the heat test.[27] The Barrow Laboratory briefly studied early ninteenth century printing ink and reached some conclusions on its effect on paper properties.[28] In view of previous studies cited, there is a question as to whether ink and/or ink/fountain solution from the modern lithographic printing process contributes to the acidity of paper and therefore whether it affects the stability of paper during storage in controlled conditions.

Theoretical Basis

During the lithographic printing process, fountain solution, which can be acidic, is emulsified by ink. This ink/fountain solution emulsion is applied to the paper. The deterioration rate of paper is affected by the amount of acid present in the paper. The source of acid can result from a source external to the paper, such as ink. This experiment addressed the question of whether ink/fountain solution emulsion has an effect on paper permanence, as determined by the retention of fold and tear properties after accelerated aging.

In order to lend itself to statistical analysis, the hypothesis is stated in the "null hypothesis" form. It is assumed that lithographic printing does not affect the permanence of paper. Permanence is affected by many factors, but in this experiment the hypothesis is narrowed to include only the effect of lithographic ink/fountain solution emulsion.

Hypothesis

This experiment examines two hypothesis:

1) There is no effect on the pH of the tested paper due to lithographic ink/fountain solution emulsion.

2) There is no measureable difference in the properties of paper tested after accelerated aging, due to lithographic ink/fountain solution emulsion.

To test the hypothesis, the experiment examines four different types of paper, printed with four different ink formulations By examining the properties of the printed and unprinted samples, before and after accelerated aging, inferences can be made about the effect of the ink formulations on the paper stability in a controlled aging atmosphere.

FOOTNOTES FOR CHAPTER II

1. A. E. Werner, "Paper Deterioration and Deacidification", presented at 1973 Seminar on the Theoretical Aspects of the Conservation of Library and Archival Material and the Establishment of Conservation Programs", Oct. 1-5, 1973, New England Document Conservation Center and the Library of Boston Athenaeum, North Andover, Mass., (c 1975), 49-75.

2. R. D. Smith, "Paper Impermanence as a Consequence of Ph and Storage Conditions", Library Quarterly, 39 (April, 1969), 154-57.

3. Ibid, 157.

4. Gosta Hall, "Permanence of Paper", Paper Trade Journal, 82 (April 8, 1926), 52-8.

5. R. W. Rasch, M. B. Shaw and G. W. Bicking, "Highly Purified Wood Fibers as Paper-Making Material", Bureau of Standards Journal of Research, 7 (August 25, 1931), 765-82.

6. Barrow Research Laboratory, Richmond, Virginia "Specifications for Permanent Durable Book Papers", American Archivist (July, 1975), 405-15.

7. Opcit, Werner.

8. Mark M. Jones, David O. Johnston, John T. Netterville, James C. Wood, Chemistry Man and Society, (W. B. Saunders Company, Philidelphia, Pa. c 1972), p. 197.

9. Opcit, Werner.

10. John C. Williams, "Paper Permanence: A Step in Addition to Alkalization", Restaurator, 3 (1979), 81-90.

11. William K. Wilson, E. J. Parks, "An Analysis of the Aging of Paper", Restaurator, 3 (1979), 37 61.

12. Opcit, Jones, 376.

13. Opcit, Wilson and Parks.

14. Opcit, Jones, 207.

15. Opcit, Wilson and Parks.

16. Opcit, Wilson and Parks.

17. B. L. Browning, *Library Quarterly*, 40 (January, 1970), p. 18.

18. David D. Roberson, "The Evaluation of Paper Permanence and Durability", *TAPPI*, 59 (December, 1976), 63-69.

19. Philip Luner, "Paper Permanence", *TAPPI*, 52 (May, 1969), 769-805.

20. Opcit, Wilson and Parks.

21. R. D. Smith, "Paper Impermanence as a Consequence of pH and Storage Conditions", *Library Quarterly*, 39 (April, 1969), p. 153.

22. Opcit, Robersen, p. 65, refer to note 37.

23. Opcit, Robersen.

24. Paul Hartsuch, *TAGA Proceedings*, 1960.

25. Opcit, Werner.

26. W. J. Barrow, *Permanence Durability of the Book-V* W. J. Barrow Research Laboratory, Richmond, Va., (c 1967). 27-29.

27. Arthur E. Kimberly, Charles G. Weber, Elmer W. Zimmerman, "Relation of Ink to the Preservation of Written Records", *Journal of the National Bureau of Standards*, 14 (April, 1935), 463-9.

28. Opcit, Barrow, p. 27, 28, 29.

CHAPTER III. METHODOLOGY

The purpose of this experiment is to study the effect of ink/fountain solution emulsion on the properties of paper as the result of accelerated aging. It is not possible to study all lithographic ink/fountain solution combinations on all types of paper. Therefore, a commonly available black lithographic ink and two fountain solutions, one acidic and one alkaline, were selected for testing on four ordinary papers. The paper obtained represents a wide range: common newsprint, uncoated book paper, coated book paper, and publication grade coated newsprint. Each type of paper was printed with four different ink/fountain solution emulsions. The ink/fountain solution emulsions were: 100% ink, 70% ink and 30% distilled water, 70% ink and 30% acidic fountain solution, 70% ink and 30% alkaline fountain solution. Appendix I contains additional information about the ink, fountain solution, and paper used in the experiment, including manufacturer, fountain solution pH, and paper basis weight.

Procedure

Ink emulsification of moisture is necessary for lithographic printing. However, the amount of fountain solution used while printing must be controlled to keep moisture emulsified by the ink at an acceptable level (up to 30%).[1] During a lithographic press run, fountain solution droplets disperse into the ink and produce a fountain solution-in-ink emulsion. If an ink emulsifies considerably more than 30% moisture it becomes "waterlogged" and can result in washed out prints.[2] However, an ink that emulsifies too little moisture is not desirable either, because the fountain solution will not mix into the ink but instead remains in droplets on the surface. This condition leads to printing that has a "snowflaky" appearance caused by the ink not reaching small plate surfaces that are protected by the fountain solution.[3]

It was necessary to decide on a standard amount of moisture to introduce into the ink for the laboratory procedure. The literature consulted stated that lithographic ink will emulsify 25% to 30% of moisture.[4] John MacPhee was more definite in "An Engineer's Analysis of the Lithographic Printing Process", (TAGA Proceedings, 1979), predicting the ink emulsified 16% fountain solution during a press run, and cited two measurements (Rosted and Madsen, 1966, and Bock 1969) that confirm this. For the purpose of this study, the author used a 30% fountain solution by weight emulsion, hypothesizing that any effect the various ink/fountain solution emulsions had on the aged paper should be more noticeable when using such a high percentage of fountain solution.

Preliminary experimentation in mixing of inks resulted in the selection of mixing ink and fountain solution by hand. A plastic container was weighed, the ink was weighed in the container, fountain solution weighing 30% of the ink's weight was measured, and the two were mixed until all of the fountain solution was dispersed into the ink. John MacPhee stated in his report[5] that most laboratory methods of introducing the moisture to the ink produces globules of moisture in the order of two to ten microns in size in contrast to the emulsified globules of moisture on a press, which could be submicron in size. In this experiment, the hand-mixed emulsion was used on a press, and printed on paper. The moisture globules were broken down by the ink rollers, and are presumed to be the size of moisture globules emulsified during a pressrun.

Paper samples were printed using an ATF Chief 15 press. A standard blanket of .065" thickness was cut to be 7" wide and the ends stripped of the rubber facing, leaving only the blanket backing on the edges. This left a 7" X 10" raised area on the blanket to print a solid on the paper samples. The prepared ink was then applied to the ink rollers and the plate inked solid so that the blanket transferred ink from the raised area onto the paper, resulting in a 7" X 10" solid area in the paper. No dampening solution, other than that in the inks, was used in the printing. The amount of ink printed on the paper samples was monitored by optical density. The densities were: 1.0 groundwood, 1.17 uncoated book, 1.5 coated book and 1.25 publication grade.

Each type of paper was printed with each of the four ink formulations. After they were printed the specimens were conditioned for one week to the laboratory atmosphere. Representative printed and unprinted samples of each paper type were aged in a forced-circulation, dry oven atmosphere at 100°C for 72 hours. After aging, the sheets were conditioned to the laboratory atmosphere again. The paper samples, both unaged and aged, were then tested using Technical Association of the Pulp and Paper Industry (TAPPI) procedures (see Appendix II). Values were obtained by testing printed and unprinted samples for folding endurance, internal tearing resistance, and acidity (pH). Appendix II describes the tests and the selection of the aging procedure in more detail.

Statistical Analysis

In this experiment, the properties of unaged and artifically aged papers were evaluated using three tests: pH determination, folding endurance, and internal tearing resistance. The results of the tests provided three sets of responses, each requiring a separate analysis. To analyze whether the result differences were caused by factor influence or experimental error, the statistical procedure "Analysis of Variance (ANOVA)" was used. The ANOVA calculation was done on the the XDS Sigma 9 computer at Rochester Institute of Technology. The subprogram "ANOVA" is part of a statistical program for social sciences, listed as "SPSS."

Table 2A shows the experimental design of the ANOVA for pH responses. This design takes into account three factors including paper, age, and ink formulation. Table 2B shows the experimental design of the ANOVA for fold and tear responses. The direction in which the paper sample is cut influences folding endurance and tearing resistance. Therefore, the ANOVA design for fold and tear responses includes direction as a fourth factor. To comply with TAPPI testing procedures, the major directional axis of machine direction and cross machine direction were selected as the levels. Paper grain direction would not be expected to influence pH, and was not included as a factor in the pH ANOVA.

The individual cells of Tables 2A and 2B include symbols indicating the combination of specific factor levels for the sample tested, with 0,

TABLE 2. LIST OF FACTORS

Factors	Levels
Direction in which sample was cut (Dir)	0 - Machine Direction (MD) 1 - Cross Machine Direction (CMD)
Paper Type (Paper)	0 - Groundwood 1 - Publication grade 2 - Coated Book 3 - Uncoated Book
Age (Age)	0 - Unaged 1 - Aged
Ink formulations printed on the paper (Ink)	0 - No Ink (plain paper) 1 - Ink 2 - Ink + Distilled Water 3 - Ink + Acidic fountain solution 4 - Ink + Alkaline fountain solution

0 2 1 3

Direction

Paper

Age

Ink

These notations would designate a tested sample as:

machine direction, coated book, aged, printed with ink/acidic fountain solution.

TABLE 2A. EXPERIMENTAL DESIGN USED FOR pH RESPONSES. Note: Paper grain direction was not a factor in the pH ANOVA. Therefore, an asterisk was substituted for the first factor of the notation in this table.

		Ground Wood	Publication Grade	Coated Book	Uncoated Book
UNAGED	No Ink	*000	*100	*200	*300
	Ink	*001	*101	*201	*301
	Ink + Distilled Water	*002	*102	*202	*302
	Ink + Acidic	*003	*103	*203	*303
	Ink + Alkaline	*004	*104	*204	*304
AGED	No Ink	*010	*110	*210	*310
	Ink	*011	*111	*211	*311
	Ink + Distilled Water	*012	*112	*212	*312
	Ink + Acidic	*013	*113	*213	*313
	Ink + Alkaline	*014	*114	*214	*314

TABLE 2B. EXPERIMENTAL DESIGN USED FOR FOLD RESPONSES AND TEAR RESPONSES

		Machined Direction (MD)				Cross Machine Direction (CMD)			
		Ground Wood	Publication Grade	Coated Book	Uncoated Book	Ground Wood	Publication Grade	Coated Book	Uncoated Book
UNAGED	No Ink	0000	0100	0200	0300	1000	1100	1200	1300
	Ink	0001	0101	0201	0301	1001	1101	1201	1301
	Ink + Distilled Water	0002	0102	0202	0302	1002	1102	1202	1302
	Ink + Acidic	0003	0103	0203	0303	1003	1103	1203	1303
	Ink + Alkaline	0004	0104	0204	0304	1004	1104	1204	1304
AGED	No Ink	0010	0110	0210	0310	1010	1110	1210	1310
	Ink	0011	0111	0211	0311	1011	1111	1211	1311
	Ink + Distilled Water	0012	0112	0212	0312	1012	1112	1212	1312
	Ink + Acidic	0013	0113	0213	0313	1013	1113	1213	1313
	Ink + Alkaline	0014	0114	0214	0314	1014	1114	1214	1314

1, 2, and 3 designating factor levels. Table 2 lists experimental factors and levels.

The experiment is not replicated. The number of factors, factor levels, and test procedures necessary to obtain a response required an impractical number of tests to produce replicate responses. Therefore, a substitute for the error term was required in order to calculate the F ratios which are the result of the comparison of variances. In the case of ANOVA, variance among the factors is compared with chance variance, or variance due to error. In order to be significant, the variance must be larger than that attributed to chance. In this experiment the highest order interaction term was used as a substitute for the error term, because the high order interaction is rarely significant.[6] This assumes no interaction effect would result among all the factors.

The mathematical model for the analysis is:

for the fold and tear responses:

$$X_{ijkl} = \mu + A_i + B_j + C_k + (AB)_{jk} + (CD)_{kl} + (AC)_{jk} + (AD)_{ij} + (BD)_{jl} + (ABC)_{ijk} + (ACD)_{ikl} + (ABD)_{ijl} + (BCD)_{jkl} + (ABCD)_{ijkl}$$

for the pH responses:

$$X_{ijkl} = \mu + B_j + C_k + D_l + (BC)_{jk} + (CD)_{kl} + (BD)_{jl} + (BCD)_{jkl}.$$

Each response or piece of data in the array is the result of: the general level (mean) of the data, μ; the possible effect associated with the different levels of the factor A (direction); the possible effect associated with the different levels of factor B (paper); the possible effect associated with the different levels of factor C (age); the possible effect associated with the different levels of factor D (ink formulations); the joint influence of the main factors, the different interactions (AB); (BC); (CD); (AC); (AD); (BD); (ABC); (ABD); (BCD); (ABCD).

FOOTNOTES FOR CHAPTER III

1. Paul Hartsuch, Chemistry for the Graphic Arts (Pittsubrgh: Graphic Arts Technical Foundation, 1979), p. 238.

2. Ibid, p. 238.

3. Ibid, pp. 238-239.

4. Ibid, p. 238.

5. MacPhee, John, "An Engineer's Analysis of the Lithographic Printing Process", TAGA Proceedings, 1979

6. Albert D. Rickmers, and Hollis N. Todd, Statistics: An Introduction. McGraw-Hill Book Company, p. 325, 1967.

CHAPTER IV. RESULTS

The data from pH determination, folding endurance, and tearing resistance tests is presented in Appendix III. Tables 3, 4, and 5 summarize these results in the experimental design. The conclusions of the ANOVA calculations for each response are presented in the ANOVA Summary Tables 6, 7, and 8. Table 9 combines the results of the three ANOVA Summary Tables into one list. Significant factors and interactions with a 95% level of confidence were designated by an asterisk.

The multiple range test was used to examine the individual factor levels and determine which levels contribute to the factor effect. Tables 10A through 10F show the multiple range test for paper and ink factors. The tables are labeled to show what factor levels are being examined and which ANOVA they are from.

In the first analysis, the response variable for fold and tear was the reported mean of ten representative samples, as directed by TAPPI Standards. Due to the variability of measurement in the fold test, it was decided to reanalyze the data using the minimum, maximum and mean values of the ten representative samples as replicates. The replication error term accounts for the range of values, or variability of measurement. Tables 11 and 12 summarize the expanded results for fold and tear. The results of the ANOVA calculations on the expanded data are presented in the ANOVA Summary Tables, 13 and 14. Table 15 combines the results into one list. Tables 16A, 16B, and 16C present the multiple range tests for

TABLE 3. SUMMARY OF EXPERIMENTAL RESULTS, pH RESPONSE.

		Paper			
Ink Treatment		Ground Wood	Publication Grade	Coated Book	Uncoated Book
UNAGED	No Ink	5.944	6.405	7.452	6.602
	Ink	5.595	6.000	7.625	5.968
	Ink + Distilled Water	5.686	6.107	7.939	6.102
	Ink + Acidic	5.645	5.731	7.512	5.958
	Ink + Alkaline	5.717	6.296	7.918	6.103
AGED	No Ink	5.630	5.743	7.381	6.125
	Ink	5.363	5.429	7.397	5.763
	Ink + Distilled Water	5.376	5.317	7.422	5.536
	Ink + Acidic	5.288	5.273	7.331	5.841
	Ink + Alkaline	5.323	5.452	7.488	5.729

TABLE 4. SUMMARY OF EXPERIMENTAL RESULTS, FOLD RESPONSE

		Machine Direction				Cross Machine Direction			
		Ground Wood	*Publication Grade	Coated Book	Uncoated Book	Ground Wood	Publication Grade	Coated Book	Uncoated Book
UNAGED	No Ink	17.7	301.8	67.8	95.0	1.6	23.5	57.0	13.3
	Ink	16.7	253.8	59.4	73.8	.7	15.1	52.9	10.6
	Ink + Distilled Water	14.6	238.1	58.6	150.7	1.6	16.4	37.7	14.5
	Ink + Acidic	16.9	219.9	59.0	79.0	1.4	13.9	57.2	11.0
	Ink + Alkaline	16.1	253.1	66.0	76.0	1.9	16.5	45.6	11.4
AGED	No Ink	18.3	214.3	48.0	65.1	1.8	16.8	42.3	12.4
	Ink	16.7	253.6	40.0	49.1	.5	16.2	35.7	9.9
	Ink + Distilled Water	15.2	133.9	35.6	124.5	1.5	12.5	44.4	15.0
	Ink + Acidic	15.5	160.9	37.9	51.4	1.6	13.3	48.5	11.4
	Ink + Alkaline	15.1	133.7	46.8	64.0	1.3	10.8	39.2	11.8

TABLE 5. SUMMARY OF EXPERIMENTAL RESULTS, TEAR RESPONSE

		Machine Direction				Cross Machine Direction			
		Ground Wood	Publication Grade	Coated Book	Uncoated Book	Ground Wood	Publication Grade	Coated Book	Uncoated Book
UNAGED	No Ink	22.0	19.65	39.30	88.80	31.75	25.75	42.05	108.20
	Ink	22.10	20.70	41.95	98.10	29.40	28.15	46.80	110.50
	Ink + Distilled Water	21.50	21.55	36.75	89.30	30.70	27.05	42.05	104.60
	Ink + Acidic	22.40	20.95	37.40	83.20	31.45	28.60	42.00	102.70
	Ink + Alkaline	20.85	21.10	38.00	81.30	30.95	27.45	42.05	102.50
AGED	No Ink	20.25	19.10	34.85	69.80	29.60	25.35	37.75	91.60
	Ink	20.35	15.45	30.95	70.10	28.45	23.95	35.40	93.40
	Ink + Distilled Water	19.85	16.70	34.75	75.80	29.75	23.50	37.20	93.40
	Ink + Acidic	19.50	16.90	35.10	77.50	29.20	23.50	38.65	92.80
	Ink + Alkaline	19.40	17.85	31.00	65.30	27.35	24.65	36.20	82.00

TABLE 6. ANOVA SUMMARY TABLE FOR pH RESPONSES

Source of Variation	Sum of Squares	DF	Mean Square	F	Significance of F
Main Effects	26.728912	8	3.3411140	491.408	--
Paper	24.561600	3	8.1871996	1204.166	*
Age	1.6403522	1	1.6403522	241.262	*
Ink	.52697033	4	.13174254	19.377	*
2-Way Interactions	.86505127	19	.045529012	6.696	--
Paper Age	.23462290	3	.078207612	11.503	*
Paper Ink	.52060318	12	.043383598	6.381	*
Paper Ink	.10981756	4	.027454391	4.038	*
Explained	27.593964	27	1.0219984	150.315	--
Residual	.81588745	12	.0067990609		
Total	27.675552	39	.70962954		

TABLE 7. ANOVA SUMMARY TABLE FOR FOLD RESPONSES

Source of Variation	Sum of Squares	DF	Mean Square	F	Significance of F
Main Effects	232444.25	9	25827.137	207.673	--
Dir	106806.69	1	106806.69	858.819	*
Paper	118658.94	3	39552.997	318.041	*
Age	5299.2539	1	5299.2539	42.611	*
Ink	1679.4021	4	419.85034	3.376	*
2-Way Interactions	139302.88	27	5159.3633	41.486	--
Dir Paper	121124.31	3	40374.770	324.648	*
Dir Age	3614.1230	1	3614.1230	29.061	*
Dir Ink	1377.6873	4	344.42163	2.769	ns
Paper Age	3900.1433	3	1300.0476	10.454	*
Paper Ink	8835.7500	12	736.31250	5.921	*
Age Ink	450.89722	4	112.72430	.906	ns
3-Way Interactions	13347.063	31	430.55029	3.462	--
Dir Paper Age	3586.4539	3	1195.4846	9.613	*
Dir Paper Ink	6986.6914	12	582.22412	4.682	*
Dir Age Ink	618.61670	4	154.65417	1.244	ns
Paper Age Ink	2155.3040	12	179.60866	1.444	ns
Explained	385094.19	67	5747.6719	46.216	
Residual	1492.3750	12	124.36458		
Total	386586.56	79	4893.5000		

ns - not significant

TABLE 8. ANOVA SUMMARY TABLE FOR TEAR RESPONSES

Source of Variation	Sum of Squares	DF	Mean Squares	F	Significance of F
Main Effects	60415.469	9	6712.8281	2475.310	--
Dir	1823.0371	1	1823.0371	672.232	*
Paper	57623.566	3	19207.855	7082.766	*
Age	887.81152	1	887.81152	327.374	*
Ink	81.053909	4	20.263474	7.472	*
2-Way Interactions	1399.0859	27	51.817993	19.108	--
Dir Paper	570.60303	3	190.20100	70.135	*
Dir Age	.25390869	1	.25390869	.094	ns
Dir Ink	1.7193708	4	.42984271	.159	ns
Paper Age	587.02734	3	195.67578	72.154	*
Paper Ink	168.38214	12	14.031845	5.174	*
Age Ink	71.099121	4	17.774780	6.554	*
3-Way Interactions	150.02734	31	4.8395910	1.785	--
Dir Paper Age	2.8407135	3	.94690448	.349	ns
Dir Paper Ink	14.240719	12	1.1867266	.438	ns
Dir Age Ink	11.781048	4	2.9452620	1.086	ns
Paper Age Ink	121.16342	12	10.096951	3.723	*
Explained	61964.582	67	924.84448	341.030	--
Residual	32.542969	12	2.7119141		
Total	61997.125	79	784.77368		

TABLE 9. COMBINED RESULTS

Source of Variation				ANOVA Summary Table pH	fold	tear
Main Effects						
Dir				na	*	*
Paper				*	*	*
Age				*	*	*
Ink				*	*	*
2-Way Interactions						
Dir	Paper			na	*	*
Dir	Age			na	*	ns
Dir	Ink			na	ns	ns
Paper	Age			*	*	*
Paper	Ink			*	*	*
Age	Ink			*	ns	*
3-Way Interactions						
Dir	Paper	Age		na	*	ns
Dir	Paper	Ink		na	*	ns
Dir	Age	Ink		na	ns	ns
Paper	Age	Ink		substituted for error	ns	*
4-Way Interactions						
Dir	Paper	Age	Ink	na	substituted for error	

na - not applicable
ns - not significant

TABLE 10A. MULTIPLE RANGE TEST OF INK FACTOR: pH

The formula for the multiple range test is

$$LSD0.05 = \sqrt{2}\ t0.025,v \sqrt{\frac{S_e{}^2}{n}}$$

where: $\sqrt{2}t_{0.025}$, is the significant studentized range; v is the degrees of freedom associated with the Mean Square for Error from the ANOVA Table; Se^2 is the mean square for error from the ANOVA Table; n is the number of cases involved in each treatment mean.

The data for ink formulations in pH ANOVA was:

$$n = 8,\ Se^2 = .0067991 \quad \sqrt{\frac{Se^2}{n}} = .029$$

The pH response mean for: no ink ($\bar{T}_1$) = 6.41

ink ($\bar{T}_2$) = 6.14

ink + distilled water ($\bar{T}_3$) = 6.19

ink + acidic fountain solution ($\bar{T}_4$) = 6.07

ink + alkaline fountain solution ($\bar{T}_5$) = 6.26

g = the number of means in a group to be compared

SSR = the significant studentized range

g	2	3	4	5
SSR	.089	.094	.097	.097

The means in arrangement according to size

$\bar{T}_4 \quad \bar{T}_2 \quad \bar{T}_3 \quad \bar{T}_5 \quad \bar{T}_1$

Note: Any two means not underscored by the same line are significantly different.

Any two means underscored by the same line are not significantly different.

Interpretation: The no-ink mean is significantly higher than the rest of the group.

TABLE 10B. MULTIPLE RANGE TEST OF INK FACTOR: FOLD

The data:

$$n = 16,\ Se^2 = 124.33333 \sqrt{\frac{Se^2}{n}} = 2.788$$

The mean fold responses no ink $\bar{T}_1 = 62.29$

ink $\bar{T}_2 = 56.54$

ink + distilled water $\bar{T}_3 = 57.18$

ink + acidic fountain solution $\bar{T}_4 = 49.93$

ink + alkaline fountain solution $\bar{T}_5 = 50.58$

g	2	3	4	6
SSR	8.59	9.01	9.28	9.37

The comparison

$\underline{\bar{T}_4\ \bar{T}_5}\quad \underline{\bar{T}_2\ \bar{T}_3\ \bar{T}_1}$

Interpretation:

The mean value for the no-ink formulation is significantly higher than the ink treated means. However, it may be similar to the ink mean and the ink + distilled water means. The ink + alkaline, and ink + acidic formulatins produced the lowest means. The differences stated are the reasons the main effect is shown to be at a significant level.

TABLE 10C. MULTIPLE RANGE TEST OF INK FACTOR: TEAR

The data:

$$n = 16,\ Se^2 = 2.7021484 \sqrt{\frac{Se^2}{n}} = .4109553$$

The mean tear responses	no ink $\bar{T}_1$	= 44.11
	ink $\bar{T}_2$	= 44.67
	ink + distilled water $\bar{T}_3$	= 44.03
	ink + acidic fountain solution $\bar{T}_4$	= 43.87
	ink + alkaline fountain solution $\bar{T}_5$	= 41.75

g	2	3	4	5
SSR	1.27	1.33	1.37	1.38

The comparison

$$\bar{T}_5 \quad \underline{\bar{T}_4 \ \ \bar{T}_3 \ \ \bar{T}_1 \ \ \bar{T}_2}$$

Interpretation:

The mean value for the ink + alkaline formulation is significantly different from the other means. The $\bar{T}_5$ mean, is the lowest of the group and was the main reason the ink effect is shown to be significant.

TABLE 10D. MULTIPLE RANGE TEST OF PAPER FACTOR: pH

The data:

$$n = 10,\ Se^2 = .0067990609 \quad \sqrt{\frac{Se^2}{n}} = .026$$

The mean pH responses:

Groundwood	$\bar{P}_1 = 5.56$
Publication Grade	$\bar{P}_2 = 5.78$
Coated Book	$\bar{P}_3 = 7.55$
Uncoated Book	$\bar{P}_4 = 5.97$

g	2	3	4
SSR	.080	.084	.087

The comparison

$\bar{P}_1 \quad \bar{P}_2 \quad \bar{P}_4 \qquad \bar{P}_3$

Interpretation:

All levels of paper are shown to be significantly different.

TABLE 10E. MULTIPLE RANGE TEST OF PAPER FACTOR: FOLD

The data:

$$n = 20, \; Se^2 = 124.36458 \quad \sqrt{\frac{Se^2}{n}} = 2.49$$

The mean fold responses:

Groundwood	$\overline{P_1}$ =	8.84
Publication Grade	$\overline{P_2}$ =	115.91
Coated Book	$\overline{P_3}$ =	48.98
Uncoated Book	$\overline{P_4}$ =	47.50

g	2	3	4
SSR	7.67	8.04	8.29

The comparison

$$\overline{P_1} \quad \underline{\overline{P_4} \;\; \overline{P_3}} \quad \overline{P_2}$$

Interpretation:

The means of the coated book paper and uncoated book paper are similar to each other. The means of groundwood and publication grade are significantly different from each other and from the two similar means, which is the reason paper is shown to be a significant effect.

TABLE 10F. MULTIPLE RANGE TEST OF PAPER FACTOR: TEAR

The data:

$$n = 20,\ Se^2 = 2.7119141 \quad \sqrt{\frac{Se^2}{n}} = .37$$

The mean tear responses:

Groundwood	$\bar{P}_1 = 25.29$
Publication Grade	$\bar{P}_2 = 22.40$
Coated Book	$\bar{P}_3 = 38.01$
Uncoated Book	$\bar{P}_4 = 89.05$

g	2	3	4
SSR	1.14	1.20	1.23

The comparison

$\bar{P}_2 \quad \bar{P}_1 \quad \bar{P}_3 \quad \bar{P}_4$

Interpretation:

All levels are significantly different.

TABLE 11. EXPERIMENTAL TABLE WITH EXPANDED FOLD DATA

		Machine Direction				Cross Machine Direction			
		Ground Wood	Publication Grade	Coated Book	Uncoated Book	Ground Wood	Publication Grade	Coated Book	Uncoated Book
UNAGED	No Ink	9.0 17.7 24.0	127.0 301.8 422.0	28.0 67.8 114.0	71.0 95.0 160.0	1.0 1.6 2.0	12.0 23.5 43.0	38.0 57.0 86.0	7.0 13.3 26.0
	Ink	7.0 16.7 28.0	150.0 253.8 346.0	45.0 59.4 87.0	38.0 73.8 143.0	.0 .7 2.0	10.0 15.1 23.0	22.0 52.9 113.0	8.0 10.6 14.0
	Ink + D. W.	4.0 14.6 29.0	118.0 238.1 378.0	28.0 58.6 113.0	91.0 150.7 286.0	1.0 1.6 2.0	8.0 16.4 26.0	19.0 37.7 58.0	7.0 14.5 24.0
	Ink + Acidic	9.0 16.9 24.0	131.0 219.9 393.0	44.0 59.0 92.0	54.0 79.0 125.0	1.0 1.4 2.0	8.0 13.9 23.0	34.0 57.2 77.0	7.0 11.0 15.0
	Ink + Alkaline	9.0 16.1 27.0	168.0 253.1 360.0	47.0 66.0 134.0	41.0 76.0 111.0	1.0 1.0 4.0	9.0 16.5 31.0	15.0 45.6 86.0	6.0 11.4 16.0
AGED	No Ink	11.0 18.3 33.0	101.0 214.3 384.0	27.0 48.0 95.0	43.0 65.1 103.0	1.0 1.8 3.0	9.0 16.8 31.0	26.0 42.3 58.0	9.0 12.4 18.0
	Ink	14.0 16.7 20.0	164.0 253.6 367.0	26.0 40.0 69.0	36.0 49.1 68.0	.0 .5 2.0	11.0 16.2 27.0	23.0 35.7 52.0	6.0 9.9 16.0
	Ink + D. W.	9.0 15.2 22.0	32.0 133.9 236.0	14.0 35.6 59.0	88.0 124.5 207.0	1.0 1.5 2.0	6.0 12.5 24.0	17.0 44.4 79.0	10.0 15.0 22.0
	Ink + Acidic	9.0 15.5 32.0	101.0 160.9 244.0	22.0 37.9 55.0	37.0 51.4 61.0	1.0 1.6 2.0	7.0 13.3 27.0	14.0 48.5 106.0	9.0 11.4 14.0
	Ink + Alkaline	10.0 15.1 25.0	72.0 133.7 212.0	28.0 46.8 90.0	44.0 64.0 80.0	1.0 1.3 2.0	7.0 10.8 16.0	24.0 39.2 51.0	8.0 11.8 16.0

TABLE 12. EXPERIMENTAL TABLE WITH EXPANDED TEAR DATA

		Machine Direction				Cross Machine Direction			
		Ground Wood	Publication Grade	Coated Book	Uncoated Book	Ground Wood	Publication Grade	Coated Book	Uncoated Book
UNAGED	No Ink	19.00 22.00 24.00	18.50 19.65 21.00	36.00 39.30 42.00	84.00 88.80 99.00	30.00 31.75 33.00	34.00 25.75 27.50	40.00 42.05 45.00	104.00 108.20 114.00
	Ink	19.50 21.10 22.50	19.50 20.70 22.00	39.00 41.95 46.00	88.00 98.10 106.00	28.00 29.40 31.00	26.00 28.15 29.50	44.00 46.80 48.00	106.00 110.50 118.00
	Ink + D. W.	20.00 21.50 23.00	20.50 21.55 23.00	35.00 36.75 38.00	85.00 89.30 93.00	29.50 30.70 33.00	26.00 27.05 29.50	40.00 42.05 43.50	100.00 104.60 108.00
	Ink + Acidic	21.00 22.40 24.50	20.00 20.95 23.00	36.00 37.40 38.50	79.00 83.20 86.00	29.50 31.45 33.50	26.50 28.60 30.00	40.00 42.00 43.00	96.00 102.70 108.00
	Ink + Alkaline	20.00 20.85 22.00	20.00 21.10 22.50	36.00 38.00 41.00	77.00 81.30 86.00	29.00 30.95 33.00	27.00 27.45 28.50	40.00 42.05 44.00	99.00 102.50 105.00
AGED	No Ink	18.50 20.25 22.00	17.50 19.10 21.00	32.50 34.85 36.50	64.00 69.80 75.00	28.00 29.60 31.00	24.00 25.35 26.50	35.00 37.75 39.50	87.00 91.60 95.00
	Ink	18.50 20.35 22.00	14.00 15.45 17.00	28.00 30.95 34.00	63.00 70.10 76.00	27.00 28.45 30.00	22.00 23.95 26.00	33.00 35.40 39.00	90.00 93.40 98.00
	Ink + D. W.	18.00 19.85 21.50	16.00 16.70 19.00	32.00 34.75 38.00	73.00 75.80 79.00	28.00 29.75 31.00	22.50 23.50 25.00	33.00 37.20 41.50	90.00 93.40 98.00
	Ink + Acidic	18.00 19.50 21.50	15.50 16.90 18.50	31.50 35.10 37.00	63.00 77.50 86.00	28.00 28.20 30.00	21.50 23.50 24.50	36.00 38.65 41.00	89.00 92.80 96.00
	Ink + Alkaline	18.50 19.40 20.50	16.00 17.85 19.00	25.00 31.00 35.00	60.00 65.30 72.00	25.00 27.35 29.50	23.50 24.65 27.00	33.00 36.20 40.00	78.00 82.00 87.00

TABLE 13. ANOVA SUMMARY TABLE FOR EXPANDED FOLD DATA

Source of Variation	Sum of Squares	DF	Mean Square	F	Significance of F
Main Effects	752180.12	9	83575.563	39.193	--
Dir	355963.63	1	355963.63	166.930	*
Paper	374043.81	3	124681.25	58.469	*
Age	17430.352	1	17430.352	8.174	*
Ink	4742.3672	4	1185.5918	.556	ns
2-Way Interactions	429292.87	27	15899.734	7.456	--
Dir Paper	371645.38	3	123881.75	58.094	*
Dir Age	11669.301	1	11669.301	5.472	*
Dir Ink	3673.2251	4	918.30615	.431	ns
Paper Age	10260.375	3	3420.1250	1.604	ns
Paper Ink	30478.246	12	2539.8538	1.191	ns
Age Ink	1566.6807	4	391.67017	.184	ns
3-Way Interactions	46369.000	31	1495.7742	.701	--
Dir Paper Age	9660.9727	3	3220.3242	1.510	ns
Dir Paper Ink	24949.875	12	2079.1563	.975	ns
Dir Age Ink	3322.3293	4	830.58228	.390	ns
Paper Age	8435.0938	12	702.92432	.330	ns
4-Way Interactions	6003.0000	12	500.25000	.235	--
Dir Paper Age Ink	6003.8086	12	500.31738	.235	ns
Explained	1233845.0	79	15618.289	7.324	
Residual	341187.00	160	2132.4187		
Total	1575032.0	239	6590.0898		

TABLE 14. ANOVA SUMMARY TABLE FOR EXPANDED TEAR DATA

Source of Variation	Sum of Squares	DF	Mean Square	F	Significance of F
Main Effects	181098.25	9	20122.027	1769.516	--
Dir	5515.1055	1	5515.1055	484.994	*
Paper	172620.88	3	57540.289	5060.051	*
Age	2726.2933	1	2726.3933	239.757	*
Ink	235.85555	4	58.963882	5.185	*
2-Way Interactions	4311.5625	27	159.68750	14.043	--
Dir Paper	1776.1326	3	592.04419	52.064	*
Dir Age	3.2471504	1	3.2471504	.286	ns
Dir Ink	5.8998041	4	1.4749508	.130	ns
Paper Age	1818.5835	3	606.19434	53.308	*
Paper Ink	510.76733	12	42.563934	3.743	*
Age Ink	196.94830	4	49.237076	4.330	*
3-Way Interactions	451.12500	31	14.552419	1.280	--
Dir Paper Age	12.408395	3	4.1361313	.364	ns
Dir Paper Ink	29.612961	12	2.4677467	.217	ns
Dir Age Ink	28.499680	4	7.1249199	.627	ns
Paper Age Ink	380.57178	12	31.714310	2.789	*
4-Way Interactions	81.312500	12	6.7760410	.596	--
Dir Paper Age Ink	81.331818	12	6.7776508	.596	ns
Explained	185942.25	79	2353.6692	206.983	
Residual	1819.4375	160	11.371484		
Total	187761.69	239	785.61353		

TABLE 15. COMBINED RESULTS

Source of Variation				ANOVA Table: Fold	ANOVA Table: Tear
Main Effects					
Dir				*	*
Paper				*	*
Age				*	*
Ink				ns	*
2-Way Interactions					
Dir	Paper			*	*
Dir	Age			*	ns
Dir	Ink			ns	ns
Paper	Age			ns	*
Paper	Ink			ns	*
Age	Ink			ns	*
3-Way Interactions					
Dir	Paper	Age		ns	ns
Dir	Paper	Ink		ns	ns
Dir	Age	Ink		ns	ns
Paper	Age	Ink		ns	*
4-Way Interactions					
Dir	Paper	Age	Ink	ns	ns

TABLE 16A. MULTIPLE RANGE TEST OF PAPER FACTOR: EXPANDED FOLD DATA

Data:

$n = 60 \quad Se^2 = 2132.4187 \quad \sqrt{\frac{Se^2}{n}} = 5.96$

The mean fold responses:

Groundwood	$\bar{P}_1$ =	9.38
Publication Grade	$\bar{P}_2$ =	119.69
Coated Book	$\bar{P}_3$ =	53.24
Uncoated Book	$\bar{P}_4$ =	51.58

G	2	3	4
SSR	16.87	17.76	18.36

The comparison

$\bar{P}_1 \quad \underline{\bar{P}_4 \quad \bar{P}_3} \quad \bar{P}_2$

Interpretation:

The means of the coated and uncoated are not significantly different from each other. All other means are significantly different. This follows the same pattern of the previous analysis on the paper factor.

TABLE 16B. MULTIPLE RANGE TEST OF PAPER FACTOR: EXPANDED TEAR DATA

Data:

$n = 60 \quad Se^2 = 11.371484 \quad \sqrt{\frac{Se^2}{n}} = .44$

The mean tear responses

Groundwood	$\bar{P}_1 = 25.31$
Publication Grade	$\bar{P}_2 = 22.46$
Coated Book	$\bar{P}_3 = 37.93$
Uncoated Book	$\bar{P}_4 = 89.01$

g	2	3	4
SSR	1.25	1.31	1.36

The comparison

$\bar{P}_2 \quad \bar{P}_1 \qquad \bar{P}_3 \qquad \bar{P}_4$

Interpretation:

All paper level means vary significantly. This is the same pattern as the previous analysis on the paper factor.

TABLE 16C. MULTIPLE RANGE TEST OF INK FACTOR: EXPANDED TEAR DATA

Data:

$n = 48 \qquad Se^2 = 11.371484 \qquad \sqrt{\frac{Se^2}{n}} = .49$

The mean tear responses

No Ink	$\bar{T}_1 = 44.14$
Ink	$\bar{T}_2 = 44.69$
Ink + Distilled Water	$\bar{T}_3 = 44.10$
Ink + Acidic	$\bar{T}_4 = 43.61$
Ink + Alkaline	$\bar{T}_5 = 41.81$

g	2	3	4	5
SSR	1.40	1.47	1.52	1.55

The comparison

$\bar{T}_5 \qquad \underline{\bar{T}_4 \quad \bar{T}_3 \quad \bar{T}_1 \quad \bar{T}_2}$

Interpretation:

There is no significant difference between the means of the no ink, ink, ink + distilled water, and ink + acidic solution treatments. The ink + alkaline solution mean is significantly different, the lowest value, and was the reason the ink factor is shown significant. These results agree with those of the previous analysis.

the expanded data.

Table 9 combines the results of each ANOVA, and shows all of the main factors (direction where applicable, paper, age, and ink) and some of the interactions are significant. It should be noted that the statistical term "significant" means "real." An effect that shows up as a statistically significant difference implies a measurable effect has been found.[1] When this occurs the null hypothesis is denied.

The main factors were included in the experimental design because this study examined the effect of ink/fountain solution emulsions on the aging behavior of paper. The paper properties pH, folding endurance, and tearing resistance were response variables. Although ink was the primary factor investigated in this study, the experimental design necessitated the other factors. Four types of paper were studied to determine if the ink/fountain solution emulsion's effect varies with paper. The design also included age as a factor in order to determine the effect aging had in the three response variables. Because the direction in which a paper sample is cut could influence fold and tear responses, grain direction was included as a factor.

pH Responses

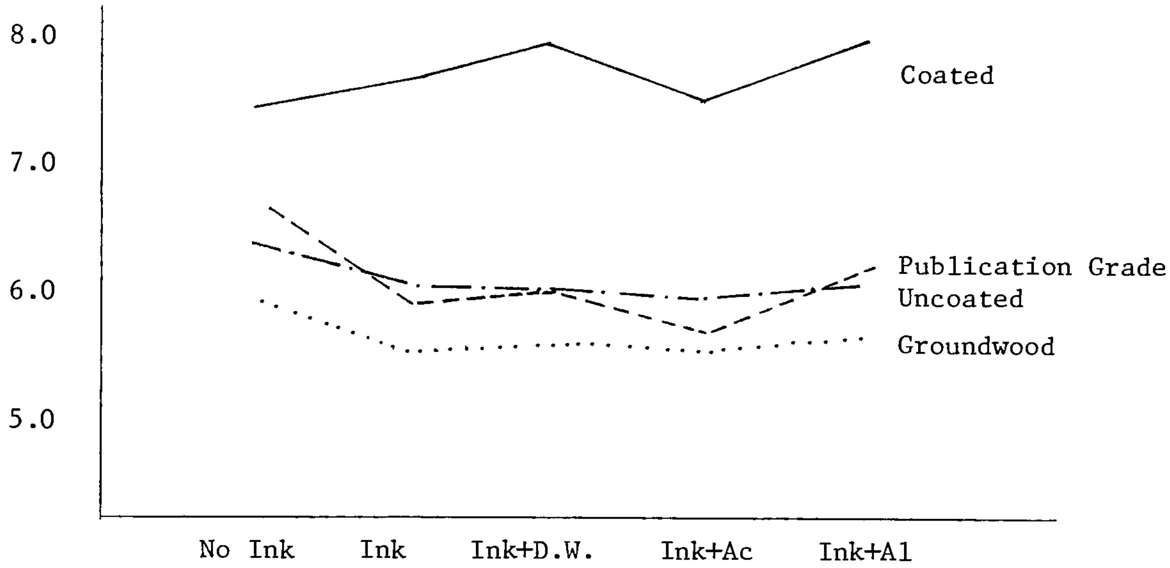
The ANOVA Summary table for pH responses, Table 6, shows paper to have a significant effect on the pH response. For the paper factor to be significant at the 95% level of confidence the calculated F ratio must exceed the tabulated F ratio, which in this case is 3.49. The calculated F ratio is 1204.17 indicating the null hypothesis must be denied. This means that there is a significant difference in the pH response due to paper. The initial consideration when choosing the papers was to select papers that were presumed to have a different pH. Therefore, the paper factor significance was an expected result. A further analysis of the paper factor using the multiple range test indicates that the mean pH of each paper type tested is at a significantly different level.

Past research has shown a decrease in the pH response after artificial aging of paper.[2] The results of this experiment agree with these earlier investigations and show age to have a significant effect on the pH response (Table 6). In order for age to be significant at the 95% level of confidence, critical F ratio required is 4.75, and the calculated age factor F ratio was 241.26.

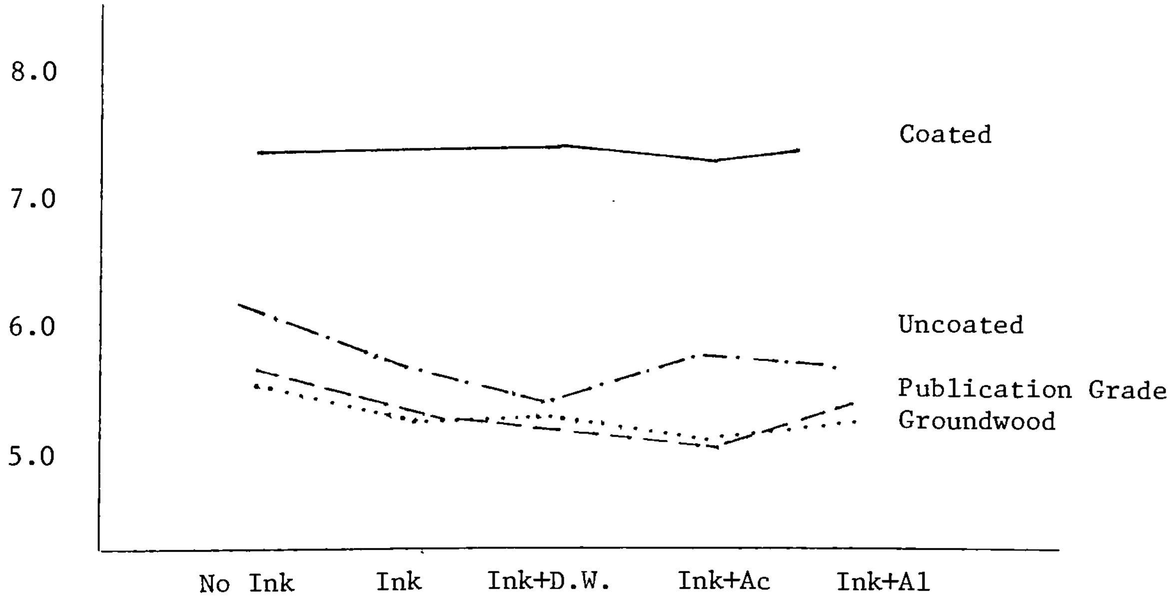
In the ANOVA, ink is shown to have a significant effect on the pH response. In order for ink to be significant at the 95% level of confidence, the critical F ratio to be exceeded is 3.26 and the calculated ink factor F ratio was 19.38. Using the multiple range test to further analyze the ink factor, the mean of the unprinted samples are shown to be significantly different from the means of the printed samples (Table 10A). The printed samples are shown to be similar to each other. Graphing the pH values illustrates the level and relative difference between the four paper types at each level of the ink factor (Figure 2). The plotted points display a pattern of variation but do not necessarily indicate a functional relationship between pH and the ink factor. The graph demonstrates in the cases of groundwood, publication grade, and uncoated book that the pH values for the printed samples are lower both in unaged and aged specimens. The graph of the coated book paper shows a higher pH

Figure 2. Graphical analysis of ink and paper, pH responses

Unaged



Aged



value for some of the unaged and aged printed samples.

The ANOVA Summary table for pH responses, Table 6, also shows the following two-factor interactions to have a significant effect on the pH response: paper/age; paper/ink; age/ink.

Fold Responses

The ANOVA Summary table for fold responses (Table 7) shows paper to have a significant effect on folding endurance. The critical F ratio required at the 95% level of confidence is 3.49 and the calculated paper factor F ratio was 318.11. Variations in paper basis weights made it probable that paper would be significant in the ANOVA results. Further analysis using the multiple range test reveals that while the means of the coated and uncoated level responses were similar, the means for groundwood and publication grade differ significantly from each other and the other two similar means.

As expected, direction had a significant effect on the folding endurance. The critical F ratio required at the 95% level of confidence is 4.75, and the calculated direction factor F ratio was 858.92. Grain direction was expected to be significant because paper offers more resistance folding perpendicular to the grain direction than paralled to the grain direction. In addition, past research has shown that artificial aging decreases folding endurance,[3] indicating that aging would also be a significant factor in this ANOVA. The critical F ratio required at the 95% level of confidence was 4.75, and the calculated age factor F ratio was 42.65. The results shown in Table 7 confirm that both grain direction and age have significant effects on the folding endurance.

The ANOVA Summary table for the fold response, Table 7, shows ink to have a significant effect on the folding endurance. The critical F ratio at the 95% level of confidence is 3.26, while the calculated ink factor F ratio was 3.38. Analysis using the multiple range test shows that the printed means are similar, but the unprinted mean is significantly different. However, the unprinted mean could be similar to the ink and the ink distilled water mean.

The ANOVA Summary table for folding endurance response, Table 7, shows the following two-factor and three factors interactions to have a significant effect on folding endurance: direction/paper; direction/age; paper/age; paper/ink; direction/ paper/age; direction/ paper/ink.

Tear Response

The ANOVA Summary table for tear responses, Table 8, shows paper to have a significant effect on the tearing resistance. The critical F ratio required at the 95% level of confidence is 3.49, and is exceeded by the calculated paper factor F ratio of 7108.82. This was expected because of the differences in the basis weights of the papers. The multiple range test shows all paper level means to be significantly different.

It was expected that grain direction would have a significant effect on tearing resistance because normally there is less tearing resistance parallel with grain direction compared to resistance across the grain direction. Past research suggests that age would also affect tearing resistance.[4] The ANOVA Summary table for tear responses Table 8, shows both grain direction and age to have a significant effect on tearing resistance. The critical F ratio at the 95% level of confidence was 4.75. The calculated F ratio of the direction factor was 675 02, and the calculated F ratio of the age factor was 328.311.

Ink is shown to have a significant effect on the tear response in the ANOVA Summary table for tear response, Table 8. The critical F ratio required at the 95% level of confidence is 3.26, and the calculated ink factor F ratio was 7.50. The multiple range test shows the ink and alkaline formulation level mean as significantly different than the other means of the factor, which are shown to be similar. The mean tear response of the ink and alkaline formulation level was the lowest of the group.

The ANOVA Summary table for tearing resistance responses, Table 8, show the following two-factor and three-factor interactions to have a significant effect on tearing resistance: direction/paper; paper/age; paper/ink; age/ink; paper/age/ink.

The folding endurance and tearing resistance testing procedures require ten representative samples be tested and the average be reported as the result. In order to consider the variability of the testing procedures, the fold and tear data was expanded to include the minimum and maximum values as replicates. This data was analyzed. The results of the analysis of the expanded data, summarized in Table 15, show all the main factors to have a significant effect on the responses, with the exception of the ink factor in the fold response ANOVA. Tables 16A, 16B, 16C show that the results of the multiple range tests for the expanded data are similar to the previous results.

Graphic Analysis

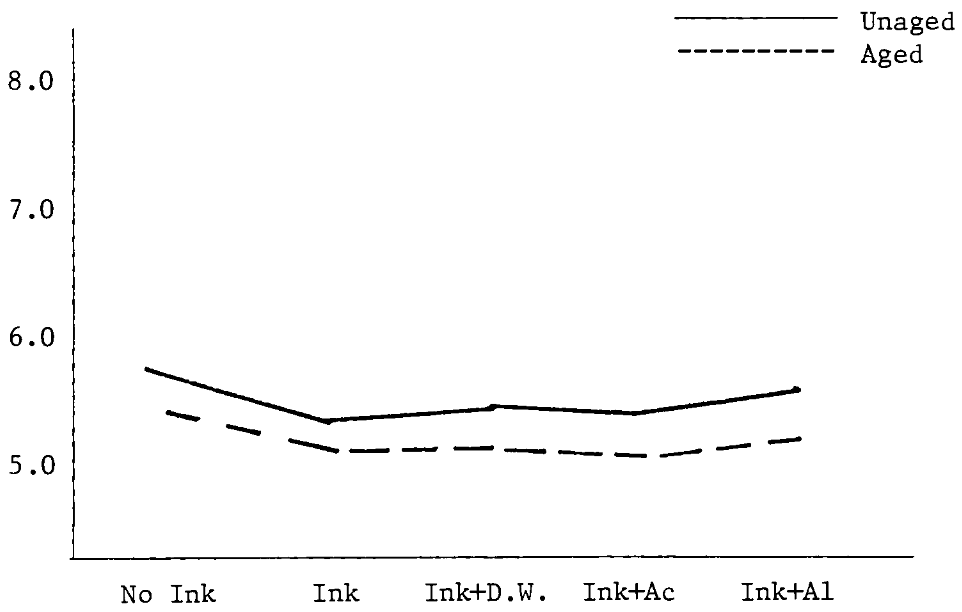
In this investigation graphical analysis demonstrates the variability of pH, folding endurance, and tearing resistance caused by the ink factor and age factor. The plotted points are joined by lines in order to display the possibility of an interaction effect between the two factors, ink and age in this case. An interaction effect is indicated if the two lines intersect or would intersect if extended. The graphs are not intended to indicate a functional relationship between the factors. Each type of paper is graphed with the response variable on the vertical axis and the factors studied on the horizontal axis.

The graphical analysis of ink formulations and age for pH response is shown in Figures 3A and 3B. A comparison of the different ink formulations indicates that for groundwood, publication grade, and uncoated paper there is a decrease in pH due to printing. This decrease in pH is indicated before and after aging. The graph of the coated paper shows an increase in the pH response after printing. The greatest change in response is due to printing, with a less striking change due to the levels of ink treatment. The graphs also show a general level change of pH with aging for each of the paper types The pH change associated with the aging process varies with the paper type and from ink formulation to ink formulation. The graphs show that after aging the pH levels at the different ink formulations develop a different pattern and that the pH level change associated with aging is greater with some papers

Figures 4A, 4B, 4C, and 4D are a graphical analysis of ink

Figure 3A. Graphical analysis of ink and age, pH responses

Groundwood



Publication Grade

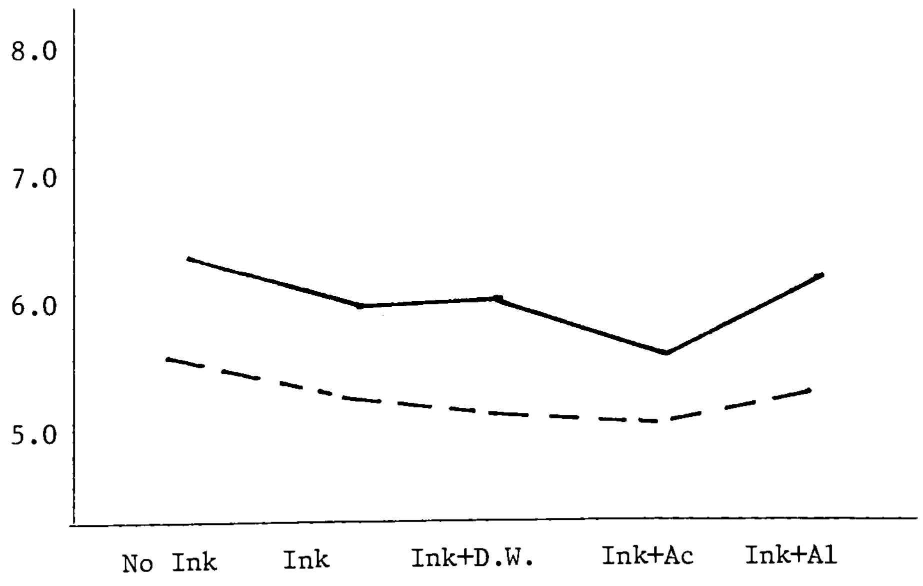
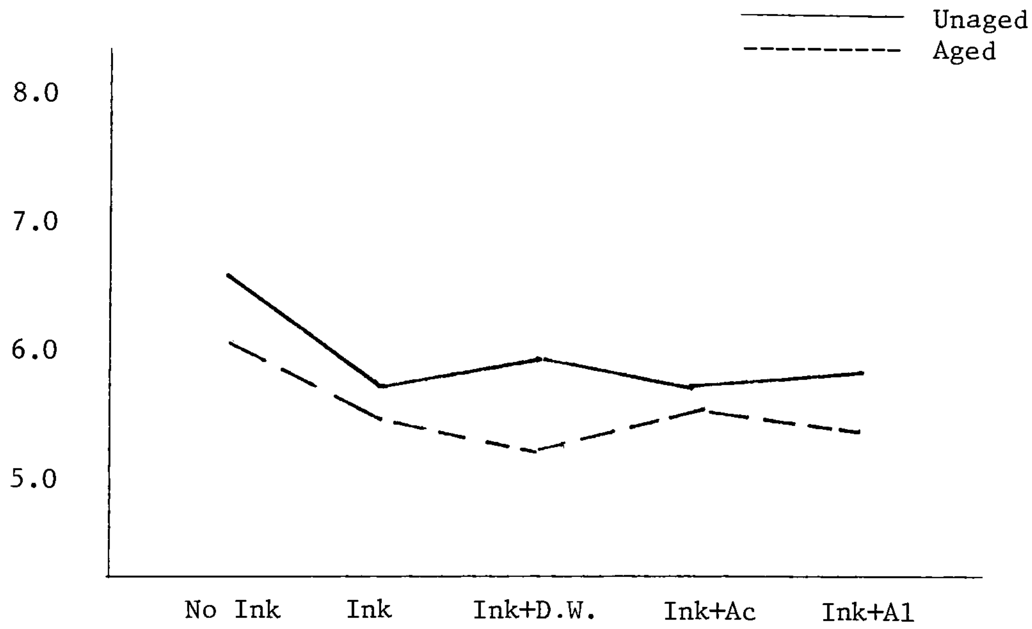


Figure 3B. Graphical analysis of ink and age, pH responses

Uncoated



Coated

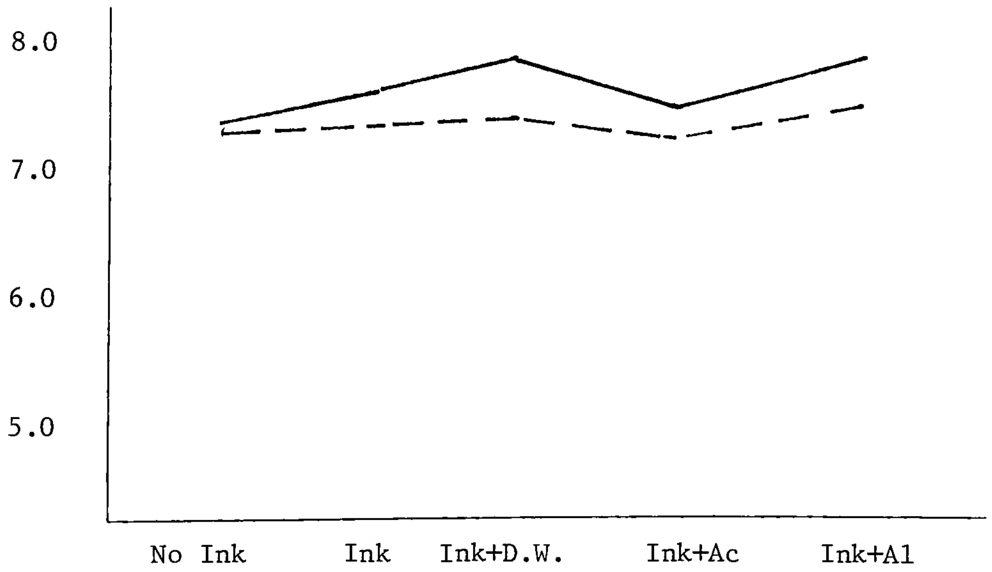
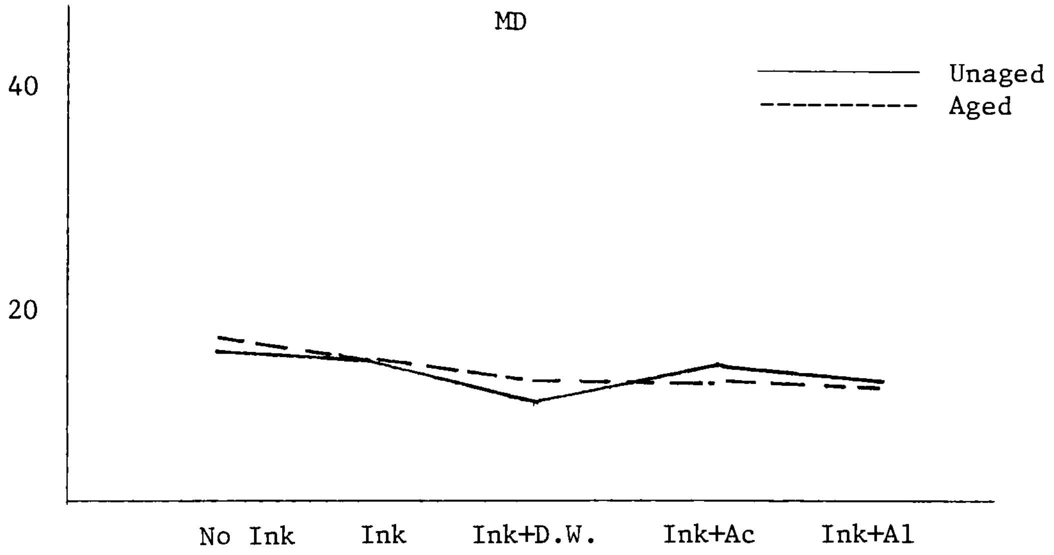


Figure 4A. Graphical analysis of ink and age, fold responses

Groundwood



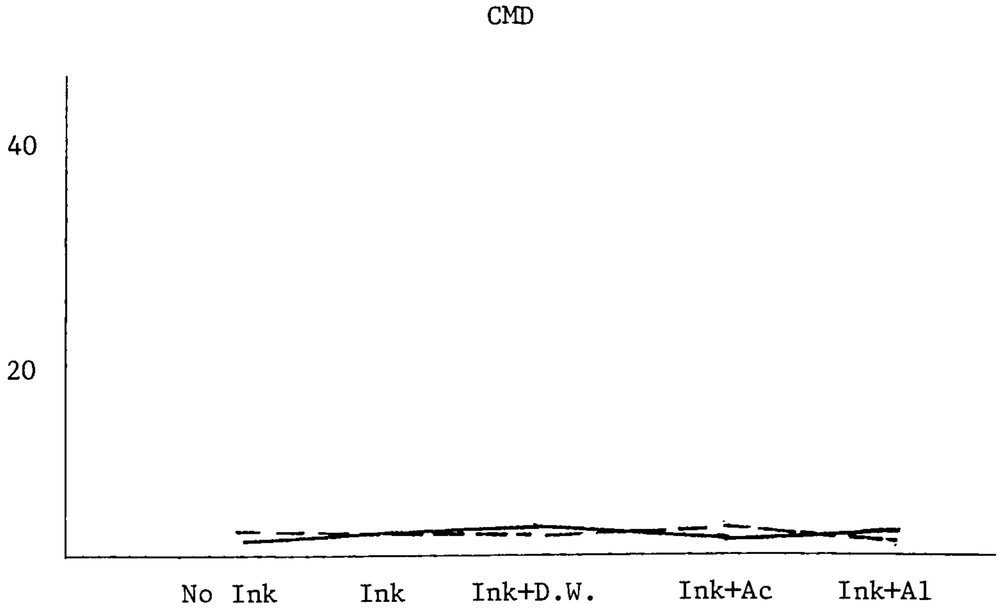


Figure 4B. Graphical analysis of ink and age, fold responses

Publication Grade

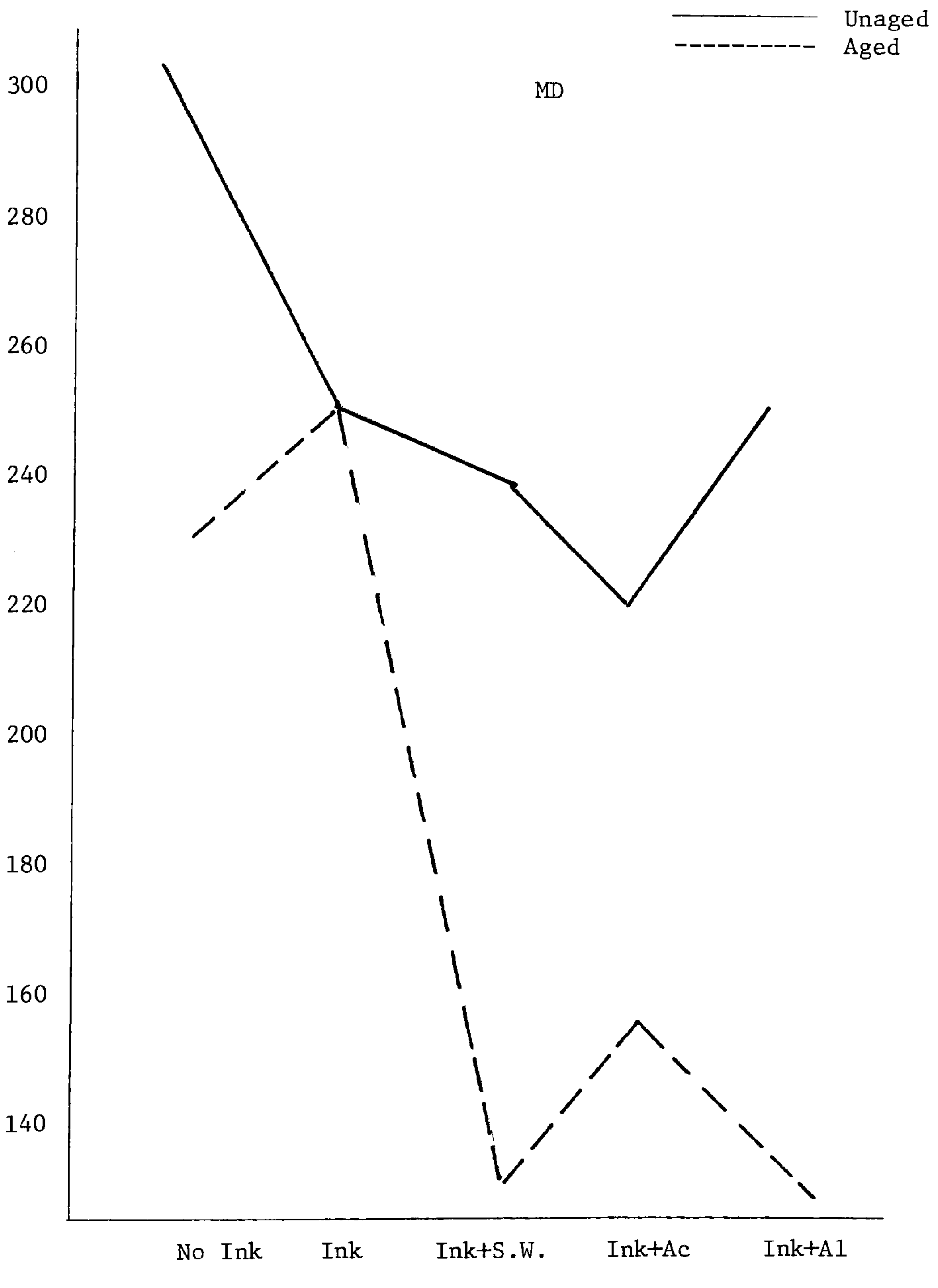


Figure 4B (continued)

Publication Grade

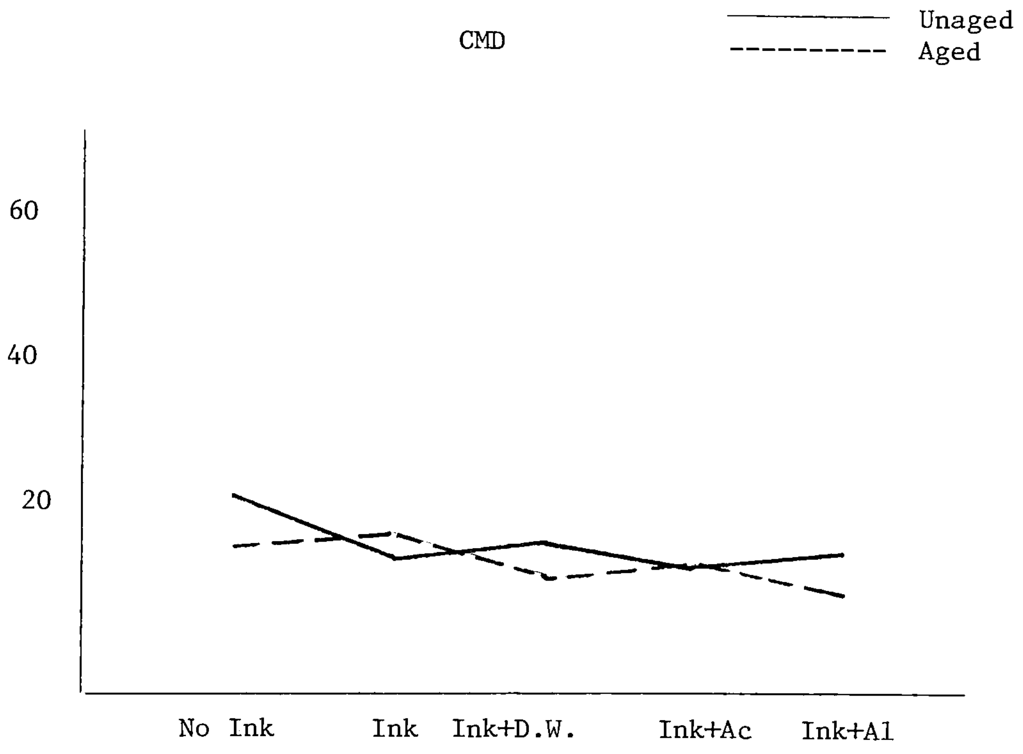


Figure 4C. Graphical analysis of ink and age, fold responses

Uncoated

MD

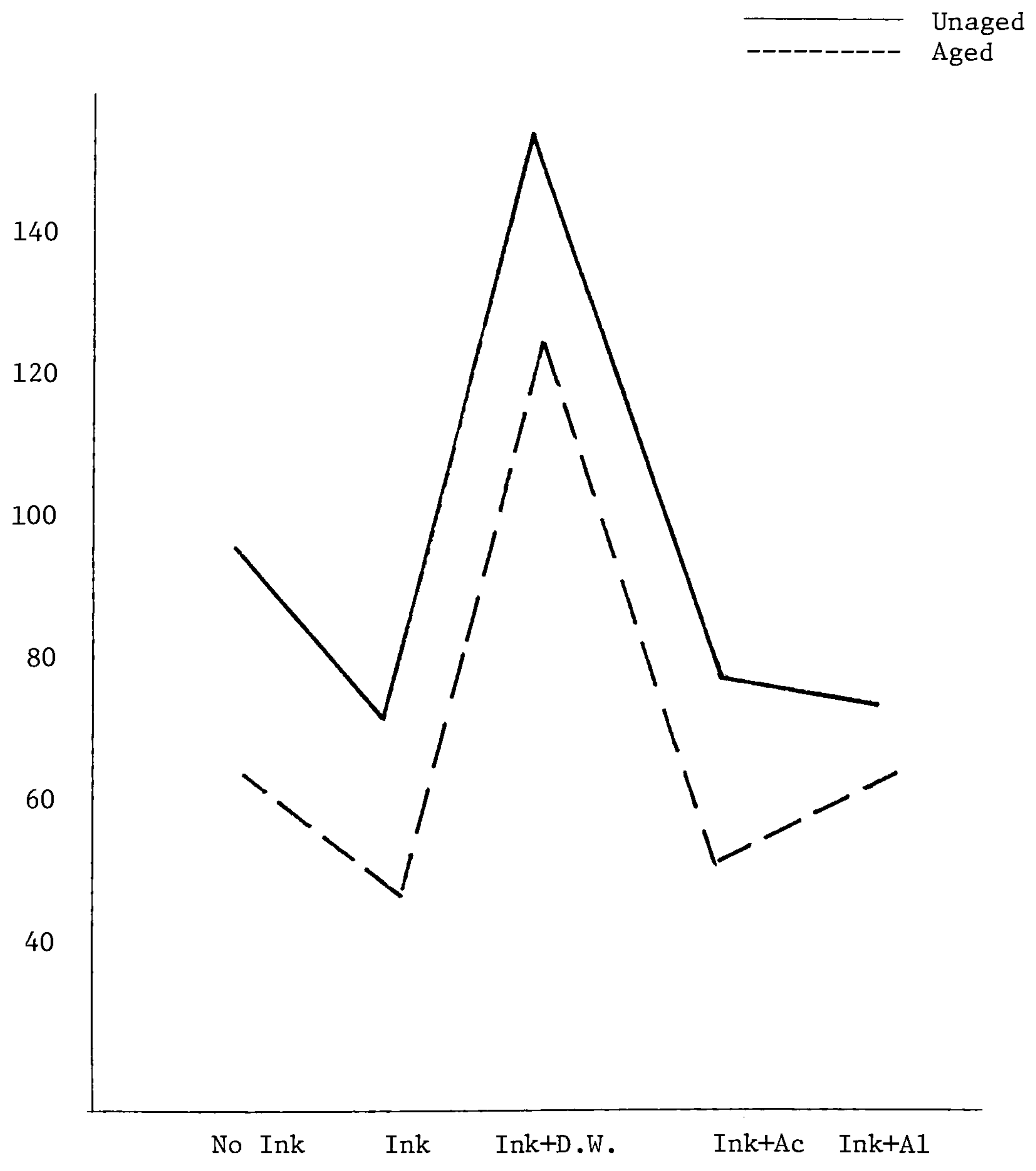


Figure 4C (continued)

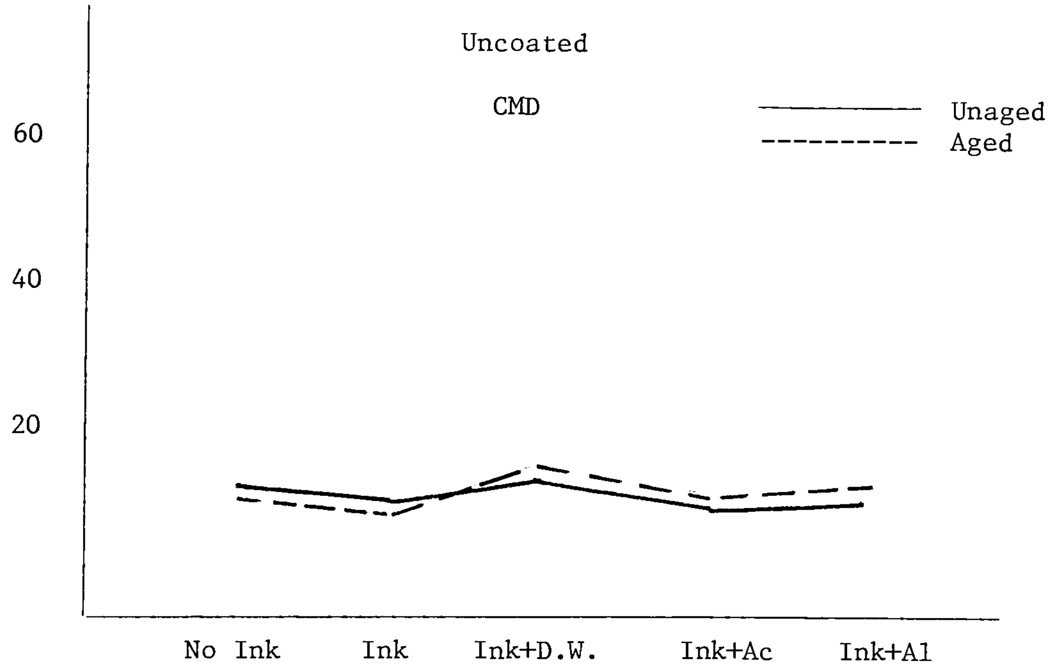
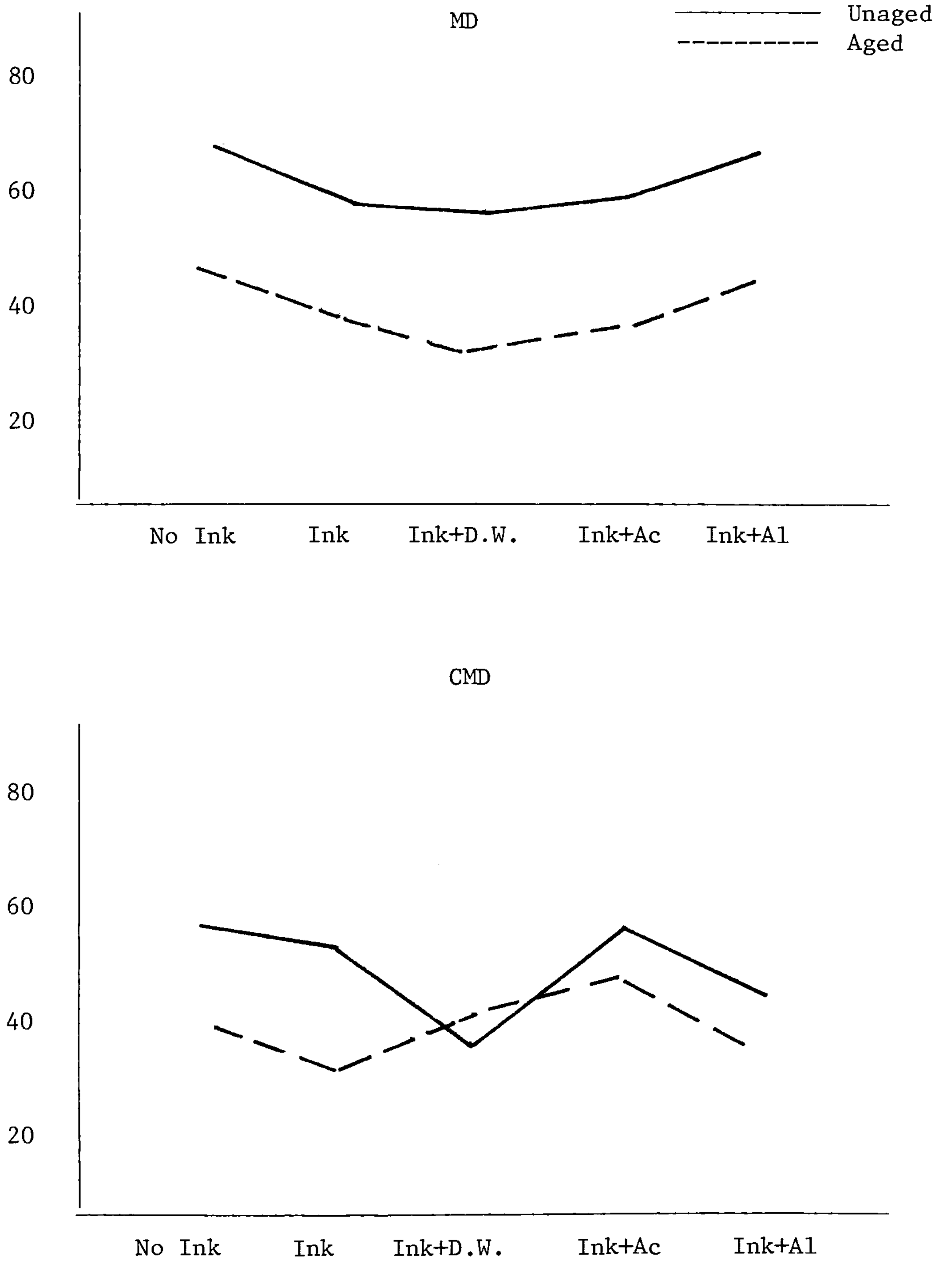


Figure 4D. Graphical analysis of ink and age, fold responses

Coated

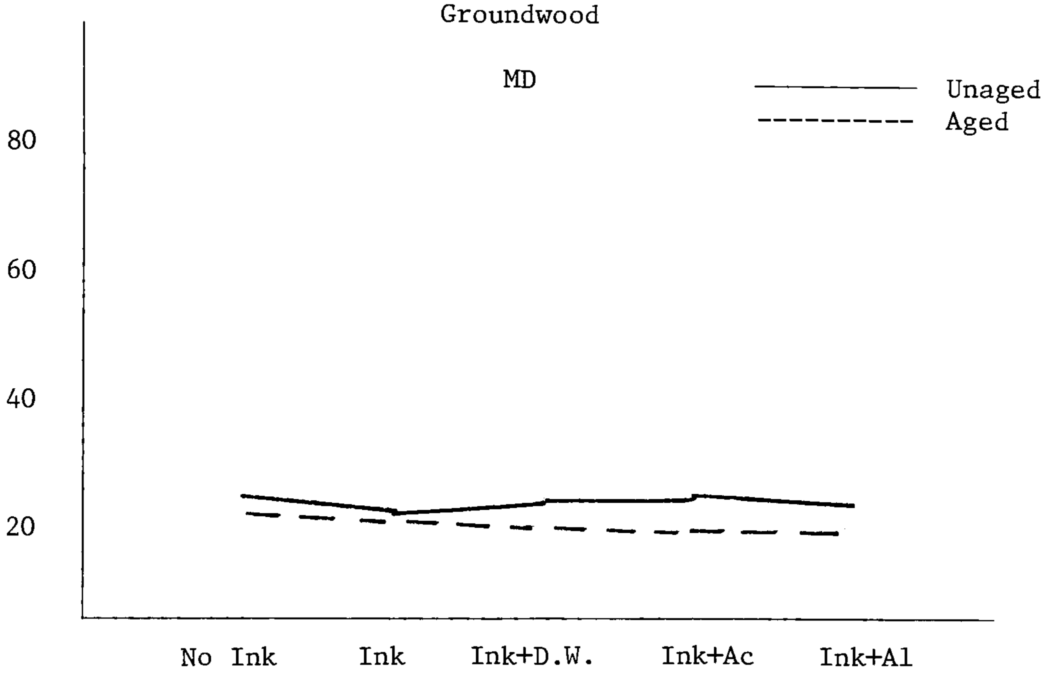


formulations and age for the folding endurance response. There is a general level change in the folding endurance associated with the aging process. This pattern is more evident with the samples folded in the machine direction when compared to those folded in the cross machine direction. However, the change associated with the aging process varies with the paper type. Groundwood exhibits almost no change in folding endurance due to aging. The effect due to the aging process also varies with the different ink formulations. The graphs of uncoated and coated papers (machine direction samples) show the general pattern of variation caused by the ink formulations is similar for unaged and aged. However, the cross machine direction samples of these two papers display a different pattern, indicating variance due to the ink formulations. The folding endurance of the uncoated and publication grade papers show differences before aging associated with the ink formulations. The results of the folding endurance test are very erratic and show no general pattern of variation common to all papers.

Figures 5A, 5B, 5C, and 5D show the graphical analysis of ink formulations and age for the tearing resistance response. It is apparent from the graphs that the general level of tearing resistance is lower for the aged samples, although the difference shown is slight for both the groundwood and publication grade papers. The graphs of the uncoated and coated papers indicate a decrease in tearing resistance associated with the ink/alkaline fountain solution emulsion and the aging process. The graphs showing the change in tearing resistance associated with the aging process appear to vary with the paper type and the different ink/fountain solution emulsions. The groundwood and publication grade papers show

Figure 5A. Graphical analysis of ink and age, tear responses

Groundwood



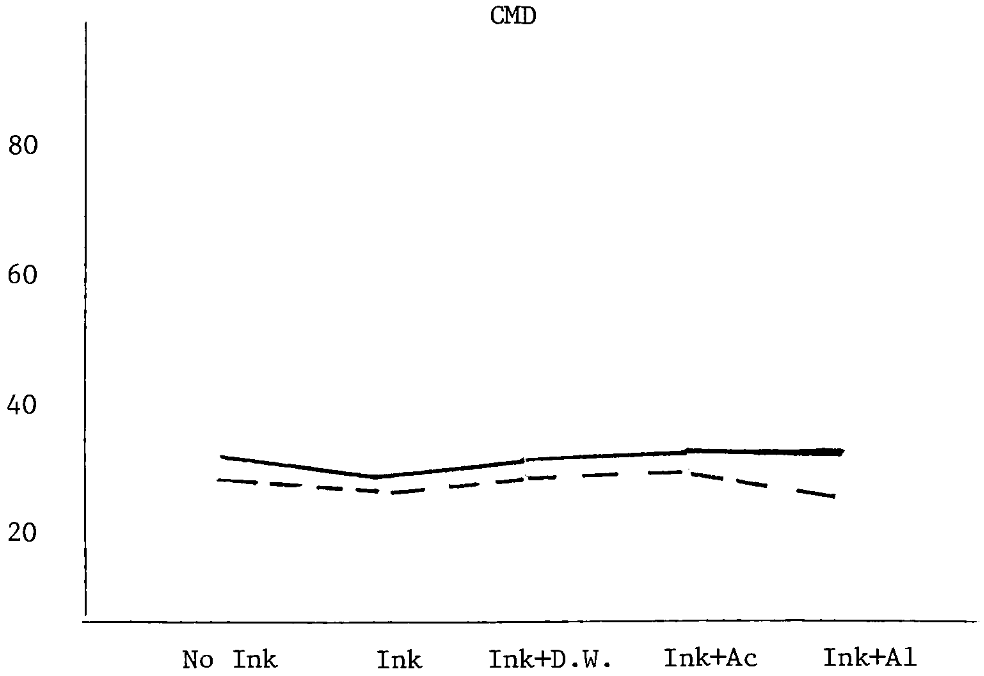
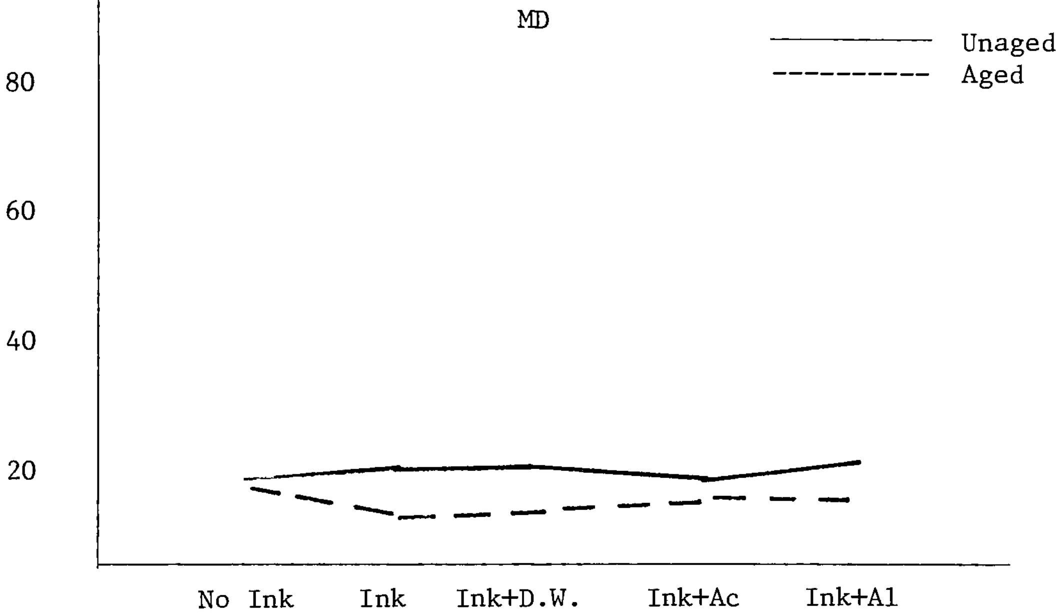


Figure 5B. Graphical analysis of ink and age, tear responses

Publication Grade



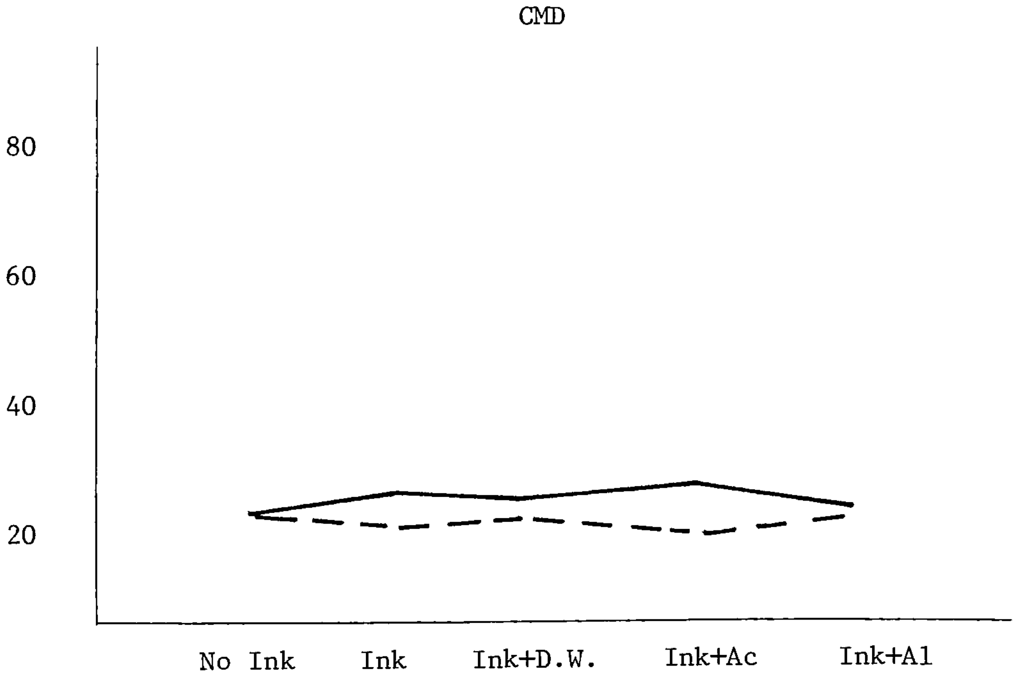


Figure 5C. Graphical analysis of ink and age, tear responses

Uncoated

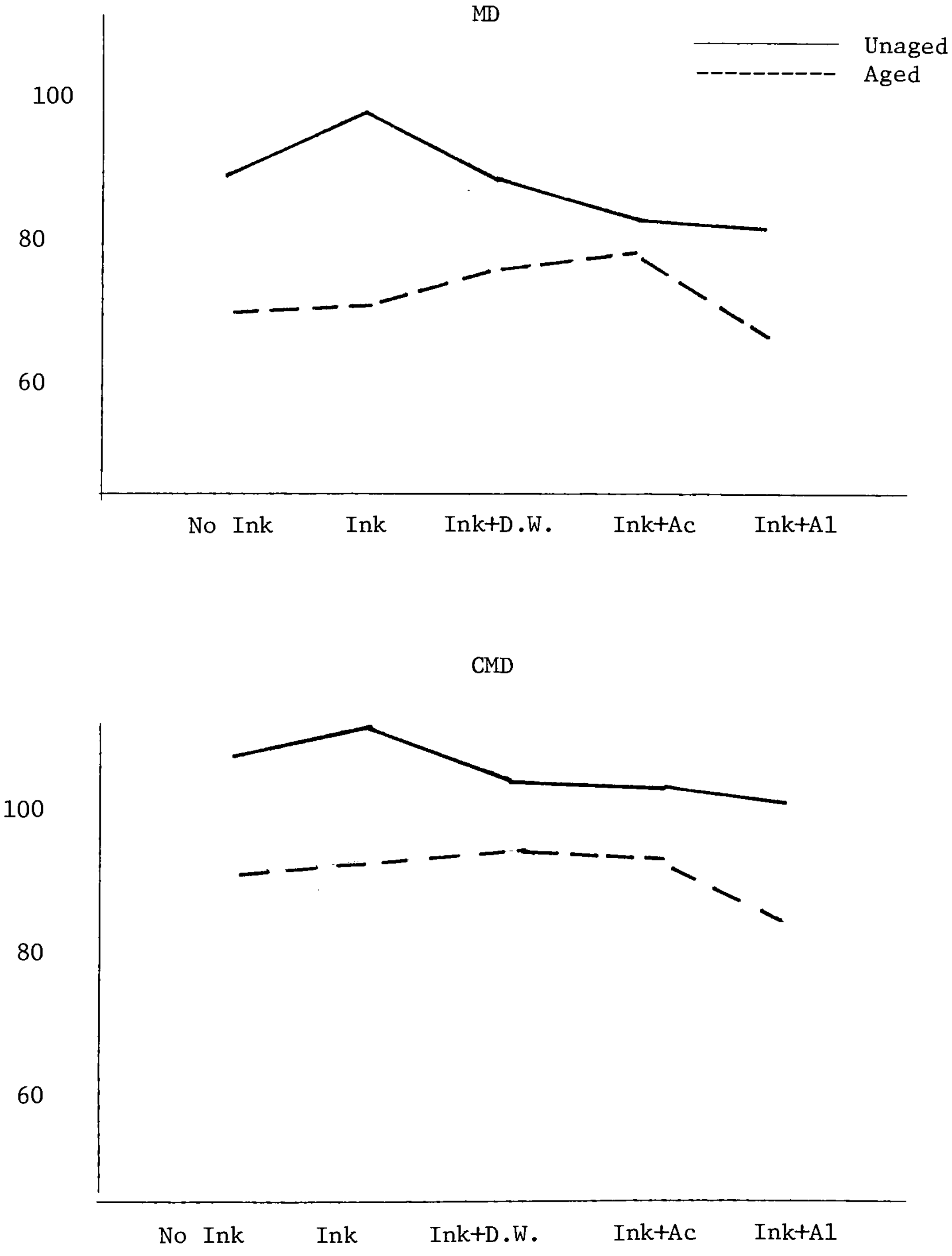
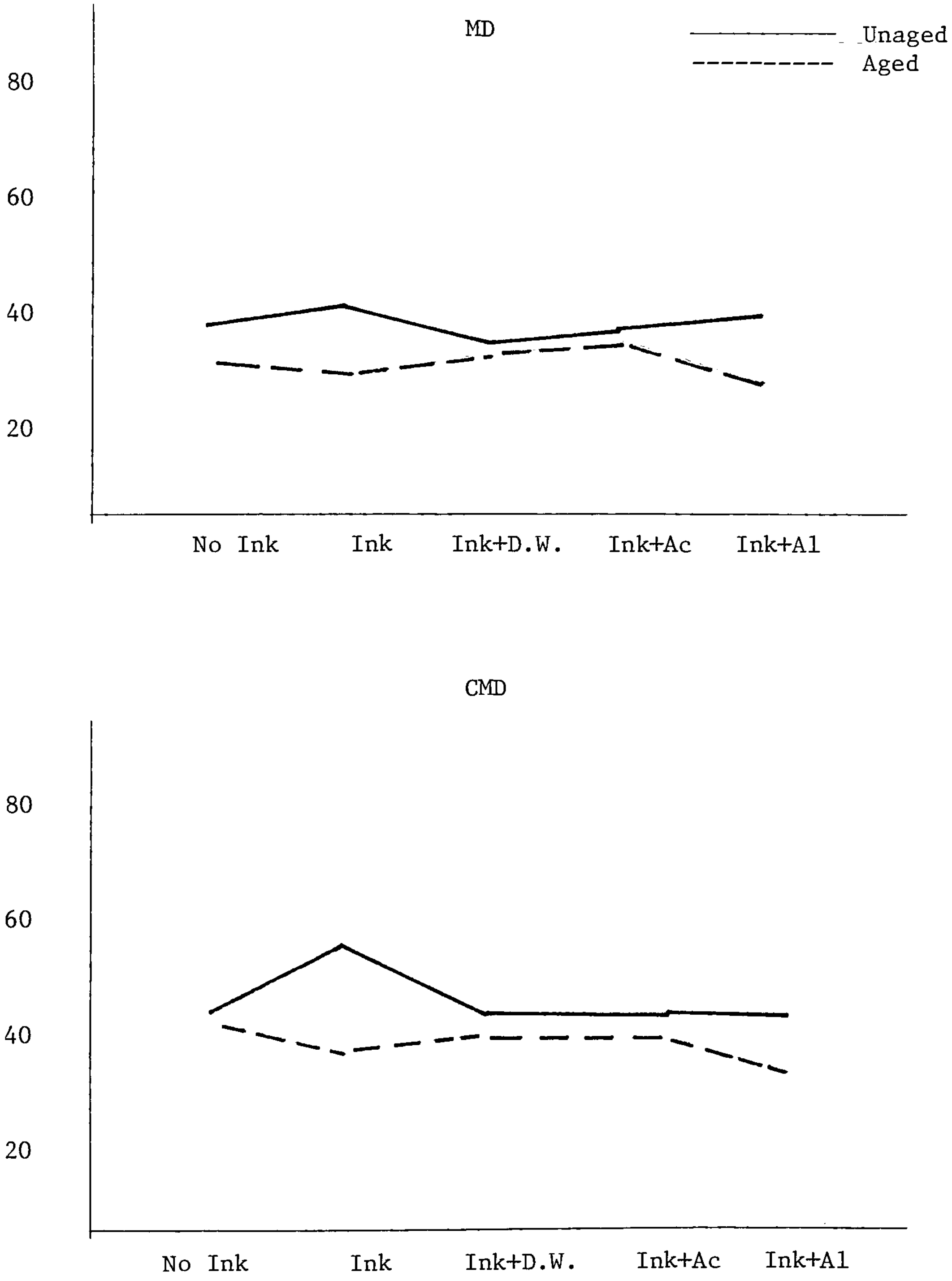


Figure 5D. Graphical analysis of ink and age, tear responses

Coated



little change with the different ink formulations, while the uncoated and coated papers show differences between ink formulations before and after aging.

Discussion of the Effects of the Experimental Factors

On the basis of the ANOVA for pH it was concluded that the paper factor had a significant effect on the pH response. On the basis of the results of the multiple range test it was concluded that this effect was due to the differences among all the paper types. Aging is shown to affect the pH response with an average decrease in this response (more acid) due to aging. The results of this experiment concluded that the pH of the paper samples decreased due to accelerated aging. This conclusion is shown by the graphs in Figures 3A and 3B and agrees with previous studies on the subject.

Although it was hypothesized that there would be no difference between the pH of the paper samples due to ink/foundation solution emulsion, the results of the ANOVA show the ink factor had a significant effect on pH response. On the basis of the results of the multiple range test it can be concluded this effect was due to the measurable difference in pH between the samples printed with the ink formulations and the unprinted samples. The multiple range test also shows that the samples printed with the different ink formulations are similar to each other. The graphs in Figures 3A and 3B show in the case of groundwood, publication grade, and uncoated book paper, there is a decrease in pH response due to the addition of the ink formulations to the paper. There is a less dramatic change than expected due to the addition of acidic or alkaline fountain solutions to the ink. The ink formulations appear to have caused an increase in the pH of the coated paper samples, which was not expected. The experiment offers no explanation for this occurence. Although a decrease was expected, this occurence is in agreement with the conclusion that ink/fountain solution emulsion affected the pH of the paper samples. It should be noted that the findings of this experiment indicate the ink factor effect on the pH response is due to the ink and not the addition of acid or alkaline fountain solution to the ink.

The graphs in Figures 3A and 3B show that changes in pH associated with the accelerated aging process vary with the ink formulations printed on the samples and also with the different types of paper. This suggests interaction effects between age and ink and between paper and age. The ANOVA shows these interactions to be significant.

The results of the fold response ANOVA show the paper factor affected folding endurance. The multiple range test indicates that the paper effect was due to groundwood and publication grade folding endurances being significantly different from each other and from the coated and uncoated paper folding endurances, which are similar.

As expected, it can be concluded from the results of the ANOVA that the direction in which a sample of paper is cut affects the folding endurance. The ANOVA also shows that age affected folding endurance, with the aging process generally causing a decrease in the folding endurance. The graphs in Figures 4A, 4B, 4C, and 4D show this by the difference in the general level of the unaged and aged responses. The accelerated aging appears to have had little effect on the groundwood paper folding endurance. Prior to testing, the author thought that the groundwood would show the greatest change in folding endurance after aging because it had the lowest pH reading. This is based on the assumption that the acidity of paper increases the rate of paper deterioration.

The results of the fold response ANOVA indicate that the ink factor produced a measureable effect in the folding endurance response of the papers tested. It can be concluded from the multiple range analysis that this effect was due to the measureable difference between the unprinted sample and four printed samples. The samples printed with the ink formulations produced significantly lower folding endurances than the unprinted sample.

Graphs of Figure 4A, 4B, 4C, and 4D indicate the change in folding endurance associated with the aging process varies with the ink formulations printed on the paper, suggesting an interaction effect between the two factors. The ANOVA of fold responses, however, indicates that this interaction was not significant. The author attributes this to the high variability in the folding endurance responses.

In the folding endurance test, the width of the paper strip folded is so small, 15 mm, that the test usually shows high variability among the ten representative samples required by the procedure.[5] "Consecutive individual tests on the same sample sometimes vary as much as 10:1."[6] In this experiment, the fold results of the different papers were very irregular and the test did not prove sensitive enough to establish a clear pattern of variation due to the age or ink factors. Based on the results of the folding endurance test the author is unable to derive firm conclusions about the effects of ink/fountain solution emulsion on the aging behavior of the paper tested.

The results of the tear response ANOVA show the paper factor has a significant effect on the tearing resistance. The results of the multiple range analysis are interpreted to indicate the four papers had measurably different tearing resistances, causing the paper factor effect to be significant.

As expected the ANOVA results indicate that direction had a significant effect on tearing resistance. Age was also indicated by the ANOVA to have a significant effect on tearing resistance. The graphical representation of the data in Figures 5A, 5B, 5C, and 5D, show that the general level of tearing resistance is less with the aged samples than with the unaged samples. The general conclusion is that accelerated aging decreased the tearing resistance of the paper.

The results of the tear response ANOVA indicate ink has a significant effect on tearing resistance. The multiple range analysis attributes this effect to the ink/alkaline fountain solution emulsion samples. The tearing resistance of the samples printed with an ink/alkaline fountain solution was significantly lower than that of the other samples. It was expected that the other ink formulations would contribute to the ink factor affect. The graphs in Figures 5A, 5B, 5C, and 5D, show the tearing resistance change association with the aging process varies with the ink formulations printed on the sheets. This suggests an age/ink factor interaction which the ANOVA indicates to be significant The graphs of the uncoated and coated paper indicate that tearing resistance after accelerated aging increased with ink/acidic fountain solution and decreased with ink/alkaline fountain solution. Prior to testing, the author expected that ink/acidic fountain solution emulsion would promote paper deterioration and decrease the tearing resistance, while ink/alkaline fountain solution emulsion would cause considerably less paper deterioration and less decrease in tearing resistance. It can be concluded that the ink/fountain solution emulsions had an effect on tearing resistance, but it appears to be the result of the alkaline fountain solution decreasing tear resistance and not the acidic fountain solution as had been thought. In general, it may be concluded that ink formulation has a significant effect on tear resistance after aging due to the significant interaction. The direction of this effect needs further study.

The data from the fold and tear tests was expanded to include maximum and minimum values as replicates. The expanded data was analyzed. The results of this analysis paralleled the prior analysis except that the ink factor was not shown to have a significant effect on the fold response.

FOOTNOTES FOR CHAPTER IV

1. Albert D. Rickmers, and Hollis N. Todd, Statistics: An Introduction. McGraw-Hill Book Company, p. 64, 1967.

2. See Chapter I, notes 1, 3, and 4.

3. See Chapter I, notes 3 and 4.

4. See Chapter I, note 3; Chapter II, note 6.

5. Chester J. Daniels, Technical and Education Center at Rochester Institute of Technology, Rochester, New York. Interview, October 27, 1981.

6. John H. Goldberger, and Robert Y. Rhyne, Sr., "A Study of the Fold Test", TAPPI, 49 (December, 1966), p. 509.

CHAPTER V. SUMMARY AND CONCLUSION

This investigation has examined the effect of ink/fountain solution emulsion on paper permanence. Printed paper products such as books and documents are expected to remain usuable over an extended period of time and require paper that has a degree of permanence equal to this period of time. This research concentrated on determining whether an ink/fountain solution emulsion printed on paper had a significant effect on the paper acidity, folding endurance, and tearing resistance before and after accelerated aging of the samples. In order not to create a unique situation, four commonly available papers were printed with four ink emulsions. These four emulsions consisted of common black Lithographic ink mixed with distilled water, ink mixed with acidic fountain solution, ink mixed with alkaline fountain solution, and the ink alone.

The paper's pH, folding endurance, and tear were tested. The three groups of results were analyzed separately using ANOVA. Conclusions about the ink factor effect on the three paper properties were drawn from the results of the ANOVA.

The first hypothesis assumes the ink/fountain solution emulsion has no effect on the pH of the tested papers. Statistical analysis of the pH responses in this experiment indicates the ink/fountain solution emulsion made a measureable difference in the pH of the printed paper samples. The multiple range test indicates that the printed samples did have significantly lower pH. However, the multiple range test and graphs in

Figures 3A and 3B also indicate that the ink, and not the addition of acidic or alkaline fountain solution to the ink, caused the largest change in pH. Although it appears to have been the ink causing the pH difference, it is concluded that ink/fountain solution emulsion did produce a difference in the pH of the paper samples and the first hypothesis is rejected.

The second hypothesis assumes there is no measureable difference in the properties of paper after accelerated aging, due to ink/fountain solution emulsion. An interaction effect between the ink factor and age factor would suggest that the ink formulations affect paper permanence and disprove the hypothesis. In order to address this hypothesis, the results of the fold response ANOVA, the tear response ANOVA, and graphical analysis of the two factors are examined.

The results of the first ANOVA for folding endurance responses indicate ink/fountain solution emulsions had a significant effect on folding endurance. The multiple range analysis indicates that this effect was due to the printed samples with little difference within the group of printed samples. It also suggests the ink and ink/distilled water formulations could yield similar results when compared to the unprinted samples in folding endurance. The graphical analysis suggests an ink/fountain solution emulsion influence on aging properties, but the ANOVA found the interaction effect to be not significant. The graphs further demonstrate that the folding endurance responses display very irregular and variable results. For example, before aging the publication grade paper displays an unexpected decrease in folding endurance due to the ink/fountain solution formulations. After aging the folding endurance increased at one point due to the ink/fountain solution formulations.

The second analysis of fold responses included expanded data to account for the high variability of the fold responses. The results of this analysis indicate the ink factor did not significantly influence the folding endurance response. Graphical analysis of the fold response shows no definite pattern of variation due to the age or ink factors. The results suggest that in this experiment the folding endurance test did not provide a clear means of determining paper permanence or detecting changes due to ink/fountain solution emulsion printed on the paper.

The results of the ANOVA for tearing resistance indicates ink/fountain solution emulsion had a significant effect on tearing resistance. The multiple range analysis shows this was due to the ink/alkaline fountain solution and not the ink/acidic fountain solution as it was expected. The graphs of the tearing resistance data show tearing resistance after aging increasing with ink/acidic fountain solution and sharply decreasing with the application of ink/alkaline fountain solution. This experiment offers no explanation for the occurrence. The graphs suggest an interaction effect between the age factor and the ink factor which is shown to be significant by the ANOVA. This indicates the effect of aging on tearing resistance in this experiment was influenced by the ink/fountain solution emulsion printed on the paper. The analysis of the expanded tearing resistance responses produced similar results.

The results of the fold test suggest that the second hypothesis should be accepted. However, the tear test results indicate the hypothesis should be rejected. Because the results of the fold and tear test demonstrated no common pattern of variability in this experiment, it is suggested that ink/fountain solution emulsion can in some cases affect certain paper properties. However, the hypothesis of no significant effect cannot be totally rejected based on the findings of this experiment.

It was expected that fountain solution difference in the ink emulsions would produce changes in the pH, fold, and tear properties. This experiment demonstrates this is not always true. The differences between the emulsions, as indicated by the multiple range tests and the graphs, were not significant and it appears any differences were due to the ink, although each paper property tested indicates different responses. It was expected that due to the differences of the pH responses, a common pattern of variability in the fold and tear responses would appear. No clear pattern was established explaining the experimental results. The results of the fold test were very erratic and the fold test did not prove to be a reliable means of indicating paper permanence for this experiment. Although the results of the tear response ANOVA indicated the ink factor could affect tear properties, the multiple range analysis and graphs indicate that this is due to alkaline and not acidic fountain solution added to the ink. The tear results also indicate that ink/fountain solution emulsion can influence the effect age has on tearing resistance. The graphs indicate this was due to the alkaline and not acidic fountain solution as expected.

It can be concluded from the results of this experiment that ink/fountain solution did affect paper pH, but that this effect was due to the ink and not due to the fountain solutions added to the ink. No clear pattern was established indicating changes in folding endurance and tearing resistance due to a change in pH caused by the ink factor.

The results of this experiment indicate the groundwood was the paper least affected by aging. The experiment also indicates a decrease in tearing resistance related to the alkaline fountain solution and an increase in pH associated with ink/fountain solution in the case of the coated paper. Because the results associated with the alkaline formulation and the coated paper were unexpected, it is recommended further study be conducted to investigate the effect of alkalinity on paper permanence.

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Appendix I

Description of Materials

Appendix I

MATERIALS

Ink

Type - Offset Lithography Ink
Brand - Superior
Company - Superior Printing Ink Company, Inc.
Color - Offset MS Premium Black A7224

Fountain Solution

Type - Acidic
Brand - Blue Polyonic
Company - RBP (Research for Better Printing) Chemical Corp.

pH - 3.09

Type - Alkaline
Brand - Automatic Dry Alkaline Mix (ADAM System)
Company - Graphic Arts Technical and Consulting Services

pH - 10.66

Distilled Water

pH - 5.94

Paper

Type	Company	Basic Weight
Groundwood (Newsprint)	International	28 lb.
Publication Grade (Coated Newsprint)	International	32 lb.
Uncoated (Book)	Pinehurst (Offset/ Smooth)	60 lb.
Coated (Book)	Champion (Javelin)	60 lb.

Appendix II

Description of Tests

Appendix II

Testing Methods·

The purpose of the paper tests selected in this study was to provide a method by which to predict the performance of the paper.

Folding Endurance:

Folding endurance was measured according to TAPPI Standard T511 by a MIT Tester. A sample of paper is cut to a width of 15 mm and a length of 13 to 15 cm. A one kilogram force is applied through a spring assembly to a jaw assembly. In order to be constant a 1-kg weight is applied to the plunger and the plunger is locked. The paper sample is clamped in the jaws of the plunger assembly and the jaws of an oscillating head assembly. The weight is removed and the plunger lock is released. The strip of paper is bent through a 270^{o} arc under the measured tension (1 kg) until it breaks. The response is recorded as the number of double folds. The paper was tested in the machine and cross machine direction. This action is meant to stimulate the bending of a leaf from a book in use. The sensitivity of this test to heat aging and the need for flexibility in book paper makes the MIT Folding Endurance Test a useful test in permanence/durability testing.[1]

Tearing Resistance:

Tear resistance was measured according to TAPPI Standard T414 by the

Elmendorf Tear Resistance Tester. The test measures, in grams, the force required to make a continuous tear through the test samples. Sixteen sheets are clamped in the tester and a slit is made to start the tear. A pendulum is released to supply the force necessary to tear the sheets. The force required to tear the sheets is measured by the loss in potential energy of the pendulum, and is indicated by a pointer. The units are grams. This test was made in the machine and cross machine direction. The action is to simulate the manner in which an individual purposely tears a sheet. This test is a commonly used test in permanence/durability testing.[2]

pH Determination:

The amount of acid present in a new paper has no effect on the physical strength at the time of testing. However, acidity can cause a gradual and continued loss of strength over time, due to the effect it has on the molecular structure of the cellulose. Therefore, a low pH value can represent potential loss of strength properties. The acidity of the paper was measured using a pH meter and the cold-extraction method as outlined by TAPPI Standard T509. Cold-extraction results have been found to correlate better with paper deterioration.[3] One gram of paper, cut into small squares, is placed in a beaker and distilled water is added. The specimen is soaked for one hour and then the unfiltered mixture is measured using a pH meter. The response is recorded as a pH number.

Accelerated Aging:

Accelerated aging was done in a forced-air circulating oven, and is often referred to as "dry oven aging". The paper samples were suspended in the oven from wires, so air could circulate between the sheets. The samples were aged for 72 hours at 100° C, which is considered equivalent to approximately 25 years. The following discussion reviews the reasons for selecting this method.

In order to study the deterioration of paper with time during storage, a method of simulating the natural aging process must be used to provide some grounds on which one might predict paper deterioration. Although interest in the permanence of paper has been present for many centuries, it was not until the beginning of the twentieth century that methods for aging and predicting paper permanence were studied in detail. While it is clear that some papers will remain in a usable condition for centuries, it is also realized that much paper, especially that produced after 1800, will not last. It is this concern that necessitates a method for "looking into the future" to see what a paper's condition will be in 10, 20, 50 or 100 years time. Hence, a means of accelerating the aging process must be used to artifically project paper, in a few days time, to the state it would be in after many years.

> "The aging of paper is due to the breakdown of the cellulose... This is a chemical reaction, and it has been known for many years that increasing the temperature enormously speeds up just about all chemical reactions."[4]

The increased deterioration of paper at higher temperatures has been used as a means of accelerating aging in tests. The National Bureau of Standards proposed that oven aging at 100° C for 72 hours equaled about 25 years and used this method in several tests run during the early 1900's. More recently, and perhaps better known, the Barrow Research

Laboratory of Richmond, Virginia, has used this method in a large number of experiments on paper permanence. This method, used by the National Bureau of Standards and Barrow Lab, is extremely low in moisture content and is widely known as the dry oven aging. However, as more has become known about paper deterioration, questions have been raised as to what adequately simulates natural aging.

The dry oven method of aging (mentioned above) is criticized for not supplying moisture during the oven heating. It has been acknowledged that moisture has a pronounced effect on the results of artifically aging paper. The results of an investigation by the National Bureau of Standards showed that moisture, either atmospheric or bound (contained in the cellulose), increased the degradation rate of paper, but an exact relationship between water and degradation was not established. In view of the effect of moisture on paper degradation, it has been suggested by Browning and Wink that all factors, including moisture, be kept constant in order to study what effects temperature does have on the rate of deterioration.[5] Methods have been developed to age papers at constant moisture by ventilating ovens with moist air or sealing samples in glass tubes, each striving for conditions that would be more nearly "natural".

The cycling of temperature and moisture during accelerated aging might more nearly duplicate natural aging. Changes in humidity and temperature may induce stresses that could accelerate loss in mechanical properties of the fibers. When the length of time that paper is stored is considered, this could have an effect on the loss of paper permanence.[6] This definitely is worth viewing as a factor to be considered when artifically aging paper. It is assumed cycling would more nearly duplicate natural aging than dry oven aging, but it has yet to be demonstrated sufficiently.[7]

In view of the above discussion, the question lingers as to what method of accelerated aging might be more nearly "natural", or meet the conditions of natural aging. To answer this, there is a need for a long term experiment in which chemical and physical tests would be run on a number of papers at intervals over many years. In 1929, the National Bureau of Standards tested a series of papers before and after accelerated aging (dry oven), and then retested additional specimens that had been stored at 4, 8, 22, and 26 years. The results of this experiment showed a fair correlation between natural aging and accelerated aging. However, because paper manufacture and testing had not advanced enough in 1928 to properly control the variables in selection of samples, only qualitative and no quantitative conclusions were drawn.[8]

In 1937, book papers made at the National Bureau of Standards were tested after accelerated aging in a circulating oven (dry oven method). The data was recorded by Shaw and O'Leary to report on the effect of fillers and sizing on book paper.[9] Some of the papers from this experiment were kept in an office for further testing later. After 36 years, eighteen of these papers were found. Since the manufacturing history and the physical and chemical properties were well documented, they were re-evaluated and the data was compared with the original data. A 1974 NBS report reviewed this data, and also the data from an experiment in which aging was done at 90° C and 50% relative humidity.

> "When data in this report are compared with data in earlier reports, it appears that dry accelerated aging more nearly corresponds to natural aging than accelerated aging at 50 percent relative humidity. The data indicates,

however, that some moisture should be present.[10]

It is apparent from the literature on the subject that a perfect correlation between natural and accelerated aging is not probable. As different storage conditions or natural aging conditions produce different results, an accelerated aging method in which conditions would meet all criteria is impossible to define.[11] In view of the above mentioned NBS report on natural and accelerated aging, and the fact that there is more documented data from dry oven aging because it is the most widely used, dry oven aging is considered an adequate method for this study. Until a definite procedure is established and standardized, including specified temperature and moisture conditions, there will be little agreement between investigations. The dry oven method, having been more widely used and documented, provides a better chance to compare experimental results with other reports and therefore to detect a trend or conclusion. The accelerated aging, therefore, will not be used to predict permanence of the samples, but rather to rank them according to properties in view or with respect to storage conditions.[12]

NOTES FOR APPENDIX II.

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2. Ibid, p. 67.

3. Barrow, W.J., TAPPI, 46 (1963), 468.

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12. Ibid, p. 56.

Appendix III

Experimental Data

TABLE 17. EXPERIMENTAL DATA OF pH DETERMINATION

	No Ink		Ink		Ink & Distilled Water		Ink & Acidic		Ink & Alkaline	
	U	A	U	A	U	A	U	A	U	A
Groundwood	5.944	5.6295	5.595	5.3625	5.686	5.376	5.645	5.288	5.717	5.323
Publication Grade	6.405	517425	6.00	5.429	6.1065	5.317	5.731	5.2725	6.296	5.4515
Uncoated	6.602	6.125	5.968	5.763	6.1015	5.536	5.958	5.841	6.103	5.749
Coated	7.452	7.381	7.625	7.397	7.939	7.422	7.512	7.3305	7.918	7.488

TABLE 18. EXPERIMENTAL DATA OF FOLDING ENDURANCE

			No Ink		Ink		Ink + D.W.		Ink + Acidic		Ink + Alkaline	
			U	A	U	A	U	A	U	A	U	A
Groundwood	MD	Min	9.0	11.0	7.0	14.0	4.0	9.0	9.0	9.0	9.0	10.0
		Mean	17.7	18.3	16.7	16.7	14.6	15.2	16.9	15.5	16.1	15.1
		Max	24.0	33.0	28.0	20.0	29.0	22.0	24.0	32.0	27.0	25.0
	CMD	Min	1.0	1.0	0.0	0.0	1.0	1.0	1.0	1.0	1.0	1.0
		Mean	1.6	1.8	0.7	0.5	1.6	1.5	1.4	1.6	1.9	1.3
		Max	2.0	3.0	2.0	2.0	2.0	2.0	2.0	2.0	4.0	2.0
Publication Grade	MD	Min	127.0	101.0	150.0	164.0	118.0	32.0	131.0	101.0	168.0	72.0
		Mean	301.8	214.3	253.8	253.6	238.1	133.9	219.9	160.9	253.1	133.7
		Max	422.0	384.0	346.0	367.0	387.0	236.0	393.0	244.0	360.0	212.0
	CMD	Min	12.0	9.0	10.0	11.0	8.0	6.0	8.0	7.0	4.0	7.0
		Mean	23.5	16.8	15.1	16.2	16.4	12.5	13.9	13.3	16.5	10.8
		Max	43.0	31.0	23.0	27.0	26.0	24.0	23.0	27.0	31.0	16.0
Uncoated	MD	Min	71.0	43.0	38.0	36.0	91.0	88.0	54.0	37.0	41.0	44.0
		Mean	95.0	65.1	73.8	49.1	150.7	124.5	79.0	51.4	76.0	64.0
		Max	160.0	103.0	143.0	68.0	286.0	207.0	125.0	61.0	111.0	80.0
	CMD	Min	7.0	9.0	8.0	6.0	7.0	10.0	7.0	9.0	6.0	8.0
		Mean	13.3	12.4	10.6	9.9	14.5	15.0	11.0	11.4	11.4	11.8
		Max	26.0	18.0	14.0	16.0	24.0	22.0	15.0	14.0	16.0	16.0
Coated	MD	Min	28.0	27.0	45.0	26.0	28.0	14.0	44.0	22.0	47.0	28.0
		Mean	67.8	48.0	59.4	40.0	58.6	35.6	59.0	37.9	66.0	46.8
		Max	114.0	95.0	87.0	69.0	113.0	59.0	92.0	55.0	134.0	90.0
	CMD	Min	38.0	26.0	22.0	23.0	19.0	17.0	34.0	14.0	15.0	24.0
		Mean	57.0	42.3	52.9	35.7	37.7	44.4	57.2	48.5	45.6	39.2
		Max	86.0	58.0	113.0	52.0	58.0	79.0	77.0	106.0	86.0	51.0

MD - Machine Direction U - Unaged
CMD - Cross Machine Direction A - Aged

TABLE 19. EXPERIMENTAL DATA OF TEARING RESISTANCE

			No Ink		Ink		Ink + D.W.		Ink + Acidic		Ink + Alkaline	
			U	A	U	A	U	A	U	A	U	A
Groundwood	MD	Min	19.00	28.00	19.50	18.50	20.00	18.00	21.00	18.00	20.00	18.50
		Mean	22.00	20.25	21.00	20.35	21.50	19.85	22.40	19.50	20.85	14.40
		Max	24.00	22.00	22.50	22.00	23.00	21.50	24.50	21.50	22.00	20.25
	CMD	Min	30.00	28.00	28.00	27.00	29.50	28.00	29.50	28.00	29.00	25.00
		Mean	31.75	29.60	29.40	28.45	30.70	29.75	31.45	29.20	30.95	27.35
		Max	33.00	31.00	31.00	30.00	33.00	31.00	33.50	30.00	33.00	29.50
Publication Grade	MD	Min	18.50	17.50	14.50	14.00	20.50	16.00	20.00	15.50	20.00	16.00
		Mean	19.65	19.10	20.70	15.45	21.55	16.70	20.95	16.90	21.10	17.85
		Max	21.00	21.00	22.00	17.00	23.00	19.00	23.00	18.50	22.50	19.00
	CMD	Min	23.00	24.00	26.00	22.00	26.00	22.50	26.50	21.50	27.00	23.50
		Mean	25.75	25.35	28.15	23.95	27.05	23.50	28.60	23.50	27.45	24.65
		Max	37.50	26.50	29.50	26.00	29.50	25.00	30.00	24.50	28.50	27.00
Uncoated	MD	Min	84.00	64.00	88.00	63.00	85.00	73.00	79.00	63.00	77.00	60.00
		Mean	88.80	69.80	98.10	70.10	89.30	75.80	83.20	77.50	81.30	65.30
		Max	99.00	75.00	106.00	76.00	93.00	79.00	86.00	86.00	86.00	72.00
	CMD	Min	104.00	87.00	106.00	90.00	100.00	90.00	96.00	89.00	99.00	78.00
		Mean	108.20	91.60	110.50	93.40	104.60	93.40	102.70	92.80	102.50	82.00
		Max	104.00	95.00	118.00	98.00	108.00	98.00	108.00	96.80	105.00	87.00
Coated	MD	Min	36.00	32.05	39.00	28.00	35.00	32.00	36.00	31.50	36.00	25.00
		Mean	39.30	34.85	41.95	30.95	36.75	34.75	37.40	35.10	38.00	31.00
		Max	42.00	36.50	46.00	34.00	38.00	38.00	38.50	37.00	41.00	35.00
	CMD	Min	40.00	35.00	44.00	33.00	40.00	33.00	40.00	36.00	40.00	33.00
		Mean	42.05	37.75	46.80	35.40	42.05	37.20	42.00	38.65	42.05	36.20
		Max	45.00	39.50	48.00	39.00	43.05	41.50	43.00	41.00	44.00	40.00

MD - Machine Direction U - Unaged
CMD - Cross Machine Direction A - Aged